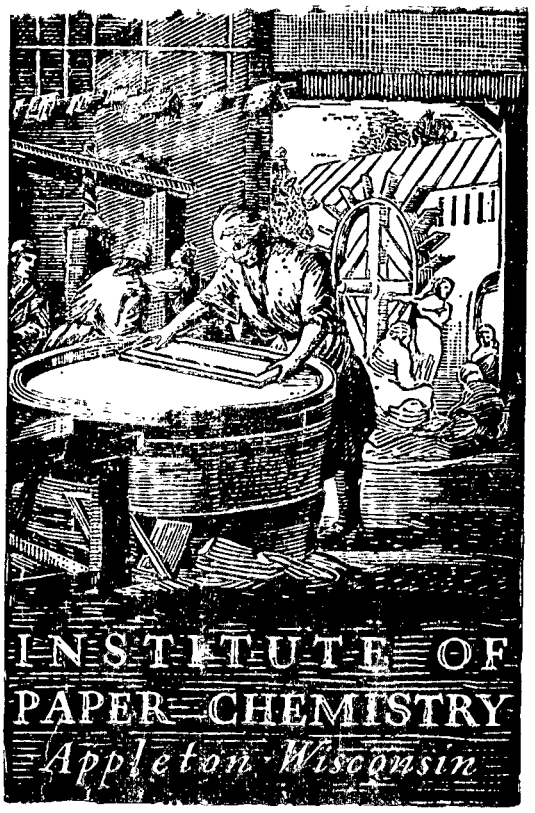
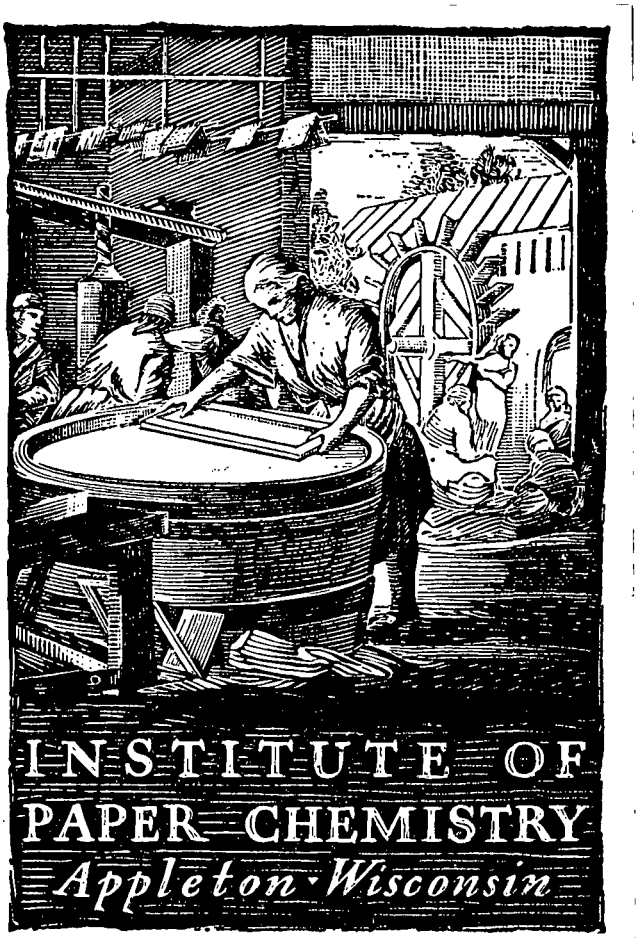


CORROSION IN HIGH YIELD PULPING PROCESSES

Project 3606

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 19, 1988



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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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ABSTRACT

Exploratory studies of corrosion rates of stainless steels (304, 316) as determined by weight loss have been completed at 90 and 150°C in alkaline sulfite, neutral sulfite, bisulfite, and acid sulfite solutions at concentrations relevant to mechanical pulping processes. The effects of NaCl and $Na_2S_2O_3$, present in pulping solutions as impurities, were investigated. Corrosion rates were very low and corrosion was more likely at pH < 7. Some severe pitting was observed in one test with the thiosulfate addition. Improved test methods must be devised to simulate vapor phase corrosion conditions.

Slow strain rate tests were performed to determine the susceptibility to stress corrosion cracking of 316 stainless steel at 150°C in the straight sulfite solutions. Conditions causing stress corrosion were not encountered in the limited number of tests completed.

This project was undertaken to provide base information for definition of a broader project to address problems which have been observed in mills. Difficulties of simulating those mill problems in controlled corrosion tests present obstacles to further research; means to overcome these obstacles must be identified before a broader project could be proposed.

SUMMARY FOR THE NONSPECIALIST

There is a lack of published information on the corrosion effects of chemical additives to TMP and CTMP processes. However, problems with cracking of steaming vessels, sulfuric acid condensation and organic acid formation have been encountered. The objective of this exploratory project has been to obtain additional information on corrosion and corrosion-assisted cracking processes occurring in mechanical pulping systems.

Corrosion rates have been measured for austenitic stainless steels (304 and 316) at 90 and 150°C in alkaline sulfite, neutral sulfite, bisulfite, and acid sulfite solutions and were found to be low. Corrosion was more likely at pH < 7. Similar behavior was found with additions of NaCl and thiosulfate ($Na_2S_2O_3$). Some severe pitting was observed in a solution with thiosulfate addition.

The polarization behavior of the stainless steels was studied to identify the range of passivity and to find any significant differences in behavior. The two stainless steels behaved similarly.

The present experimental methods were inadequate for simulating the corrosion problems encountered in the vapor phase in mill equipment. Further studies should focus on the effects of impurities and additives at high temperature (150°C).

The susceptibility of 316 stainless steel to stress corrosion cracking at 150°C has been investigated, also. At the natural corrosion potential, stress corrosion problems were not found in the straight sulfite solutions. Additional work is needed to determine the conditions which will cause chloride stress corrosion cracking in these environments.

INTRODUCTION

Despite the proliferation of high yield pulping processes and equipment, there is a lack of published information on the corrosion effects of impurities or additives to TMP and CTMP processes. Problems with chloride cracking of steaming vessels, sulfuric acid condensation and organic acid formation have been encountered.

By means of a better understanding of the range of conditions which cause corrosion, it should be possible to increase the useful life of equipment through proper selection of materials of construction and identification of suitable process conditions.

The objective of this project was to obtain basic information on corrosion and corrosion-assisted cracking processes occurring in mechanical pulping equipment to identify potential problems and solutions. The perspective of this project was to be exploratory in nature, to determine the range of sulfite environments which could cause corrosion in mechanical pulping systems.

LITERATURE REVIEW

CHEMISTRY OF TMP, CTMP AND CMP LIQUOR

Thermomechanical pulping (TMP), chemithermomechanical pulping (CTMP) and chemimechanical pulping (CMP) processes employ chemicals or heat or both to assist the pulping. The TMP processes typically use less than 1% chemical, CTMP processes have 1-5% chemical in the pulping solution and CMP processes use higher chemical concentrations. A range of chemistries with a variety of additives is found for these processes. For the purposes of this study, these chemistries will be divided into four categories: alkaline sulfite, neutral sulfite, bisulfite, and acid sulfite.

Alkaline sulfite (pH 11) and neutral sulfite (pH 7) chemistries contain sodium sulfite (Na_2SO_3) with sodium bisulfite ($NaHSO_3$) or sodium hydroxide (NaOH) components. The neutral sulfite semichemical process may contain in excess of 120 g/L Na_2SO_3, pH 9-11, 120°C, with additions of NaOH, Na_2CO_3 or $NaHCO_3$.

Bisulfite solutions contain approximately equal amounts of free and combined SO_2. These solutions have a pH of approximately 4-6. Vapor phase cooking is widely practiced in these processes. Abitibi-Price operates a process (BCMP) at Chandler using bisulfite at pH 5.8-6.4, 600 kPa, 168°C and 6-9% SO_2 in an M & D digester.[12,13] Bisulfite is also added in MacMillan-Bloedel's CTLF process.[17] Consolidated-Bathurst operates an ultra high yield vapor phase pulping process at Grand'Mere which uses Na_2SO_3.[14]

Acid sulfite solutions are made by absorbing SO_2 into a base such as limestone, milk of lime, magnesium hydroxide, sodium hydroxide or ammonia.

Ammonium, sodium and magnesium based compounds are the most popular bases. The SO_2 in solution forms a mixture of H_2SO_3, HSO_3^- and SO_3^{2-}. The total SO_2 in the liquor is about 6%. The pH of these solutions is very low: about 1.5 to 2.

The different sulfite species are present in proportions which depend on the pH. Below pH ~2, SO_2 predominates. From pH 2 to ~7.3, bisulfite is the predominant ion, and above pH ~7.3, the sulfite ion is most stable.[21]

Temperatures in TMP are generally up to 120-130°C. Chips are presteamed at temperatures above 100°C. The chips are then fed to the first stage refiner at a pressure to maintain temperatures at 120-130°C. Second stage refining is usually conducted at atmospheric pressure. In CTMP, the chemical is added to the chips prior to or during presteaming at temperatures above 100°C.

Additives are added just before the refiner in many processes to brighten the pulp, buffer the pH or improve plate life. Hydrogen peroxide and hydrosulfite (dithionite) are added to bleach the pulp. Bisulfite is added to brighten the pulp. Sodium sulfite is sometimes added to reduce refiner plate corrosion.[5] Sodium carbonate additions may be made to control pH to about 6.

CORROSION PROBLEMS

Corrosion in Sulfite Solutions

McGovern[8] has reported intergranular corrosion in acid sulfite and bisulfite pulping digesters. Thorpe[10] and Potter, Kesler and Teeple[11] have also noted this problem if the alloy is sensitized. The extent of this problem in CMP or CTMP processes is unknown.

McGovern[7,8] has noted that bisulfite decomposition is autocatalytic, one of the catalysts being thiosulfate which is formed during the decomposition.

The net reaction is:

$$HSO_3^{2-} \longrightarrow 2\ SO_4^{2-} + H^+ + S + H_2O$$

Intermediate reaction products include polythionate derivatives which, under conditions of excess acidity and high temperature, ultimately yield H_2SO_4 and S. McGovern linked corrosion problems in spent sulfite liquor handling to systems with degraded spent liquor. Condensation of H_2SO_4 from spent bisulfite liquor caused failure of 304 and 316 stainless steel storage tanks.

Vapor Phase Corrosion

Vapor phase corrosion[1,12,14,15] has been observed in a number of mills using processes which have pH < 6. Inconel 625[14] and 904L have been used to overcome this. Sulfuric (H_2SO_4) and sulfurous (H_2SO_3) acids cause very serious problems in presteaming vessels. Charlton[1] has observed pitting of 316 stainless steel and has suggested that Na_2SO_3 used in the process was decomposing at the high temperature in the refiner to form SO_2 which was flowing back to the steaming vessel to form H_2SO_3. There was evidence that acid was condensing on surfaces and streaming down the sides. On the other hand, sulfurous acid solutions are oxidizing in nature and so 316 stainless steel should be fairly resistant, but sulfuric acid may dissolve the protective oxide film and cause rapid attack.[11] Brophy[23] has reported that stress corrosion can occur in sulfurous acid, with the SO_2 acting as an accelerator. Murarka[12,15] has described severe corrosion problems due to H_2SO_4 formed in the digester vapor space of a bisulfite CMP process. The concentration of acid formed depended on the liquor pH and the amount of oxygen present in the reactor.

Charlton[1] suggested that polythionic acid may be forming. It is known to be a very aggressive corrodant. Polythionic acid affects sensitized austenitic stainless steel alloys only, so should not be a problem most of the time. Stabilized stainless steels and special shutdown procedures are employed in refineries to prevent stress corrosion by polythionic acid. There is some question whether it is formed; Murarka[16] was unable to detect it in condensate formed during lab tests or taken from operating digesters. On the other hand, it may have an effect at low concentrations below the minimum for analysis.[23]

The contamination of weak solutions of sulfuric acid with SO_2 can increase the critical current values for passivation (the active/passive peak) by more than two orders of magnitude for 304 stainless steel, with similar results for type 316, 430 and 18Cr-2Mo stainless steels.[19] This would make it more difficult for the steels to passivate. Also it has been suggested that the lowering of the pitting potential by SO_2 could be attributed to the lowering of pH by formation of H_2SO_3 and to acceleration of active dissolution by the action of the H_2S formed. In contrast, Ahlers[9] has obtained results which indicate that steels remain passive to corrosion as long as there is some free SO_2 present. Recently, Zamaletdinov et al.[22] examined the effect of SO_2 in NaCl solutions (2 g/L Cl^-) on stainless steels. Pitting intensified with increases in temperature from 20-50°C. A small concentration of SO_2 (2.4 g/L) inhibited pitting. This indicated that pitting could occur during the time cooked pulp remains in a batch digester after the final relief.

Additives or Impurities

Specific corrosive species in the process may cause corrosion in TMP and CTMP equipment. These species include chloride, hydrosulfite, organic acids and inorganic acids.

A major source of problems is the sodium hydrosulfite (dithionite) used for bleaching.[5] It decomposes to thiosulfate and bisulfite which stimulate corrosion of the paper machine.[2,17] Similar problems would be anticipated in the stainless steels in the pulp mill. Thiosulfate is known to cause stress corrosion of sensitized stainless steels.[24] Moreover, the thiosulfate will stimulate the decomposition of bisulfite. In spite of all this, Barton[4] has claimed that 316 and 317 stainless steel are sufficiently corrosion resistant to the hydrosulfite bleaching environment in a refiner. Up to 0.4% thiosulfate has been measured in low yield acid sulfite processes at pH 3.5-4, and some may be anticipated in the high yield processes.

Chlorides, another corrosive species, may be brought in with logs transported by sea or by brackish water. Recycled bleach plant effluents are another source. Evaporation may also concentrate small amounts of salt. Laliberte[2] has noted the importance of chlorides to pitting and crevice attack in mechanical pulping. Localized attack of 316 stainless steel can occur in sulfite processes with high chloride concentrations. Both 316 (with 2.75% Mo) and 317 stainless steels may be satisfactory in some cases, but severe localized attack and stress corrosion cracking have been observed even on 317L in the presence of > 1000 ppm chloride. Ahlers[9] has noted that chloride will cause activation and consequently higher corrosion rates. Charlton[1] has reported an instance of chloride stress corrosion cracking in a 316 stainless steel vertical expansion joint used in a TMP operation. Another source[3] has encountered failure of a 316 steaming vessel in a TMP plant due to chloride SCC. A replacement constructed of 904L subsequently failed and had to be replaced with Hastelloy 276. Cracking has also been observed in a refiner shroud of 14-4 PH stainless steel and in casings of CF8M.

Organic acids arising in the wood may also cause corrosion. White water may have a pH of 4-6 due to fatty and resin acids.[2] Franzen[6] has noted that the low pH of condensates indicates the presence of organic acids. Ahonen[20] noted that the steam exiting from a TMP refiner contains several organic acids, notably formic acid. Organics may act as inhibitors in sulfite liquors,[18] although there is no information for the concentrations typical of mechanical pulping systems.

Temperature

Higher temperatures would be expected to increase corrosion rates. Temperatures of 40-60°C are encountered in cold grinding and 60-90°C in hot grinding. The maximum temperature is about 135°C in open discharge mechanical pulping but may be up to 160°C at 100 psi.[2] Higher pressures will, in general, accelerate corrosion. General increases in temperature also accompany recycling.

Wear

Corrosion and wear of refiner plates occurs through a combination of erosion accelerated by the corrosive environment, as well as cavitation caused by localized flashing of water to steam.[1,2] As temperatures increase, cavitation may become more of a concern.

OUTSTANDING QUESTIONS

Lower pH apparently leads to an increase in corrosion problems. There is a need to define what corrosion problems are anticipated in different ranges of pH and sulfite concentration. Determination of the range of conditions under which sodium sulfite is corrosive was the focus of this study.

Problems can also occur in the vapor phase, but the mechanism of vapor phase attack is not known. Condensation of sulfuric acid is known to be a serious problem but the conditions for its formation are not well defined. Polythionic acid cracking may be a problem in the vapor phase but almost no information is available concerning it.

Chlorides in the process can have a significant negative effect on materials performance. Other additives, for example hydrosulfite, cause corrosive conditions but the sensitivity to these constituents is not known.

Many questions remain. What is the optimum chemistry from a corrosion point of view? What operating conditions can cause corrosion problems? Are the present materials of construction the best choices? What is the cause of stress corrosion in these processes? This study has been directed toward answering some of these questions.

EXPERIMENTAL

SOLUTION COMPOSITION

Deoxygenated, distilled water and analytical reagents were used to prepare the solutions. To prevent air oxidation, nitrogen blanketing was used during mixture and handling. The target compositions are listed below.

Straight Sulfite Solutions

i) Alkaline Sulfite
   a) 8 g/L Na_2SO_3 - pH adjusted to 10 with NaOH
   b) 12 g/L Na_2SO_3 - pH adjusted to 10 with NaOH

ii) a) 15 g/L Na_2SO_3 - pH adjusted to 7 with $NaHSO_3$
   b) 65 g/L Na_2SO_3 - pH adjusted to 7 with $NaHSO_3$

iii) Bisulfite
   a) 12 g/L $NaHSO_3$ - pH adjusted to 4 with SO_2
   b) 30 g/L $NaHSO_3$ - pH adjusted to 4 with SO_2

iv) Acid sulfite
   30 g/L $NaHSO_3$ - pH adjusted to 1.5 with SO_2

Additions

i) 1 g/L NaCl
ii) 5 g/L $Na_2S_2O_3$

Chemical Analysis

Sulfite solutions used in the study were analyzed by ion chromatography to determine their actual composition. The analyses are summarized in Table 1. Thiosulfate was not detected in any of the liquors. The analysis for Na_2SO_3 and $NaHSO_3$ is reported in terms of Na_2SO_3. At pH 1.5, substantial additions of SO_2 were made to acidify the solution. This accounts for the high concentration of Na_2SO_3 in the acid sulfite solution. Small amounts of SO_2 added at pH 4 seemed to have negligible influence on composition. Significant degradation of the liquor was observed after two weeks, as noted in Table 1.

Table 1. Chemical composition of test solutions.

Target Composition	Actual Composition	After 2 Weeks
8 g/L Na_2SO_3 pH 10	5.98 g/L Na_2SO_3 0.59 g/L Na_2SO_4	
12 g/L Na_2SO_3 pH 10	8.34 g/L Na_2SO_3 1.11 g/L Na_2SO_4	
15 g/L Na_2SO_3 pH 7	16.57 g/L Na_2SO_3 1.04 g/L Na_2SO_4	4.01 g/L Na_2SO_3
65 g/L Na_2SO_3 pH 7	58.7 g/L Na_2SO_3 2.66 g/L Na_2SO_4	
12 g/L $NaHSO_3$ pH 4	10.02 g/L Na_2SO_3 0.44 g/L Na_2SO_4	7.2 g/L Na_2SO_3 4.1 g/L Na_2SO_4
30 g/L $NaHSO_3$ pH 4	26.4 g/L Na_2SO_3 0.89 g/L Na_2SO_4	14.8 g/L Na_2SO_3 13.6 g/L Na_2SO_4
30 g/L $NaHSO_3$ pH 1.5	52.4 g/L Na_2SO_3 1.1 g/L Na_2SO_4	

Corrosion was studied at 90 and 150°C. Additions of NaCl and $Na_2S_2O_3$ were studied in selected sulfite solutions at 90°C. The effects of additions were not studied in weight loss tests at 150°C due to termination of the project.

EQUIPMENT

Testing at 90°C was done in 500 mL fluorinated ethylene propylene (FEP) jars in a temperature controlled steam bath. Each jar contained 4 cylindrical stainless steel test electrodes: two 304 SS and two 316 SS. The composition of the steels is given in Table 2. One electrode of each material was immersed in the solution, and the other was exposed in the vapor phase as illustrated in Fig. 1. The temperature in the vapor phase was approximately 75°C. It was

hoped that condensates would form at this lower temperature and that the specimen would be further cooled by the electrode holder which was held by a steel screw extending outside of the cell. The electrodes had a surface area of 9 cm^2. The electrode holders were constructed of polytetrafluoroethylene (PTFE), and the electrodes were isolated from the holder by ethylene propylene gaskets. The electrodes were polished to 120 grit prior to the test.

Table 2. Composition of stainless steels.

Steel	C	Si	P	S	Cr	Mn	Ni	Cu	Mo	Co	Fe
304	0.06	0.32	0.023	0.027	18.32	1.66	9.96	1.03	0.38	--	bal
316	0.05	0.33	0.026	0.026	16.28	1.47	11.17	0.22	2.84	0.07	bal

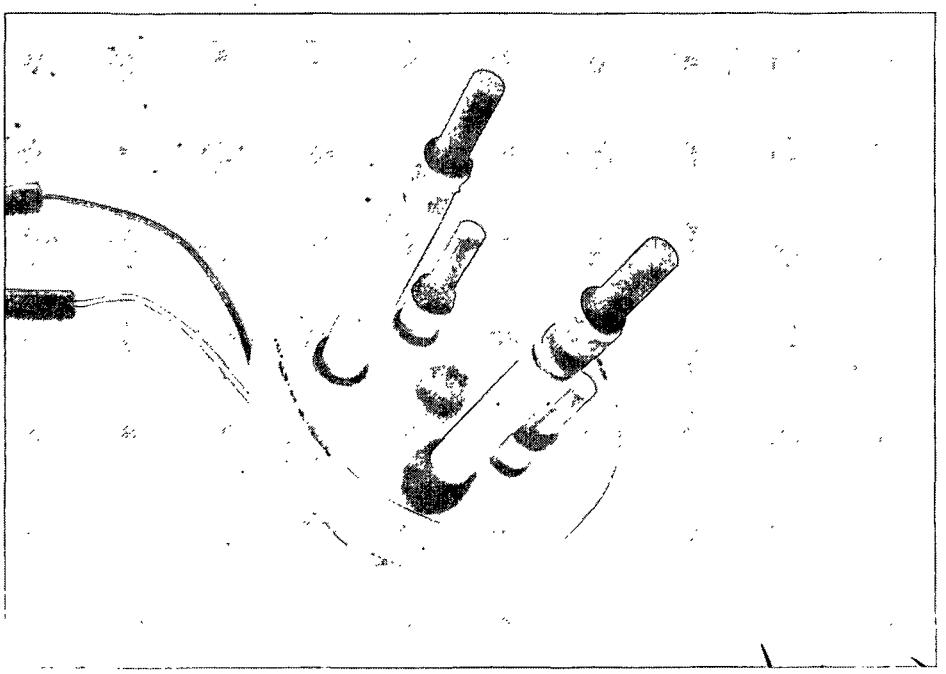

Figure 1. Test electrodes were exposed in both the liquid and the vapor phases.

Measurements of electrode potential were made with a standard calomel electrode or silver-silver chloride reference electrode (SSCE) with a salt bridge. Electrode potential was measured daily. Test solutions were changed at 2 week intervals. Polarization curves were obtained using a Princeton Applied Research Model 350 Corrosion Measurement System scanning at 1 mV/s. Before the scan was started, the electrode was cathodically polarized at -1.0 V_{SSCE} for 15 minutes to reduce species on the surface. Polarization curves were obtained at 150°C using a 316 SS autoclave with an external silver-silver chloride reference electrode. A graphite counter electrode was used in all tests. In the test at pH 1.5, 150°C, an N_2 + SO_2 atmosphere was placed over the solution to preserve the SO_2 in solution. Weight loss tests at 150°C were conducted in a Hastelloy C276 autoclave.

A Hastelloy C276 autoclave including grips for slow strain rate testing was constructed for use at 150°C. It is illustrated in Fig. 2. The slow strain rate test is widely used to measure susceptibility to stress corrosion cracking. In the test, a cylindrical tensile specimen is pulled slowly to failure. A relatively short test ending in brittle failure indicates susceptibility to stress corrosion cracking; a long test ending in ductile failure indicates that the material is not susceptible. The slow strain rate apparatus is illustrated in Fig. 3. The apparatus was manufactured by TW Specialty Co. and included a variable speed motor which is connected to the main worm gear through two speed reducer gear boxes to provide a constant strain rate of 2×10^{-6} sec^{-1}. The pull rod entered the top of the autoclave via a Conax PG5-750-AT seal. The autoclave also had a seal for a thermocouple probe and nitrogen inlet tube. Heating of the autoclave was provided by two external 675 W Chromolux heating coils.

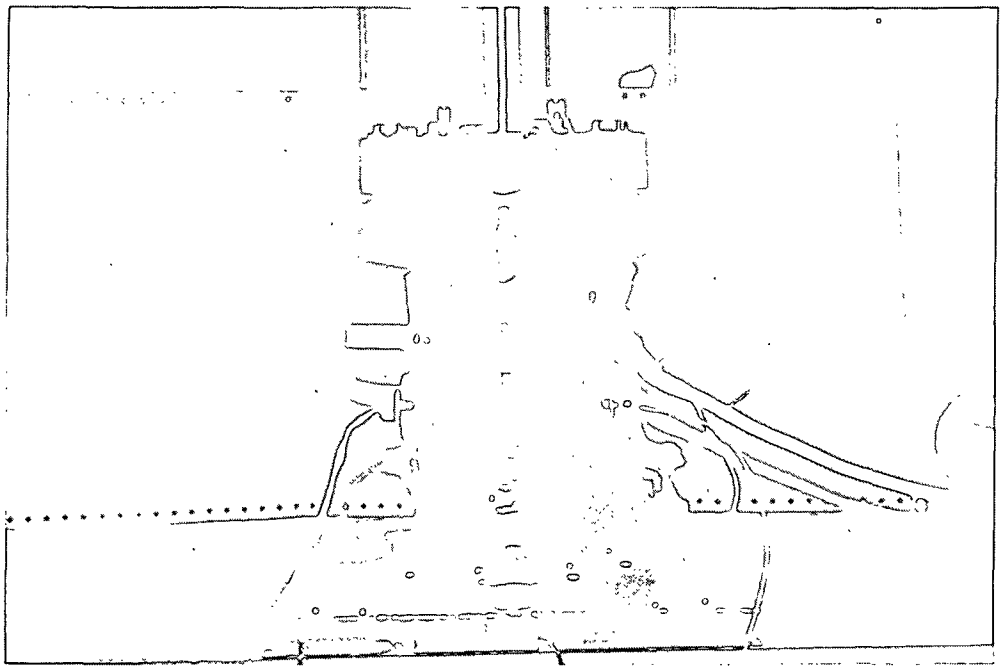

Figure 2. Hastelloy autoclave.

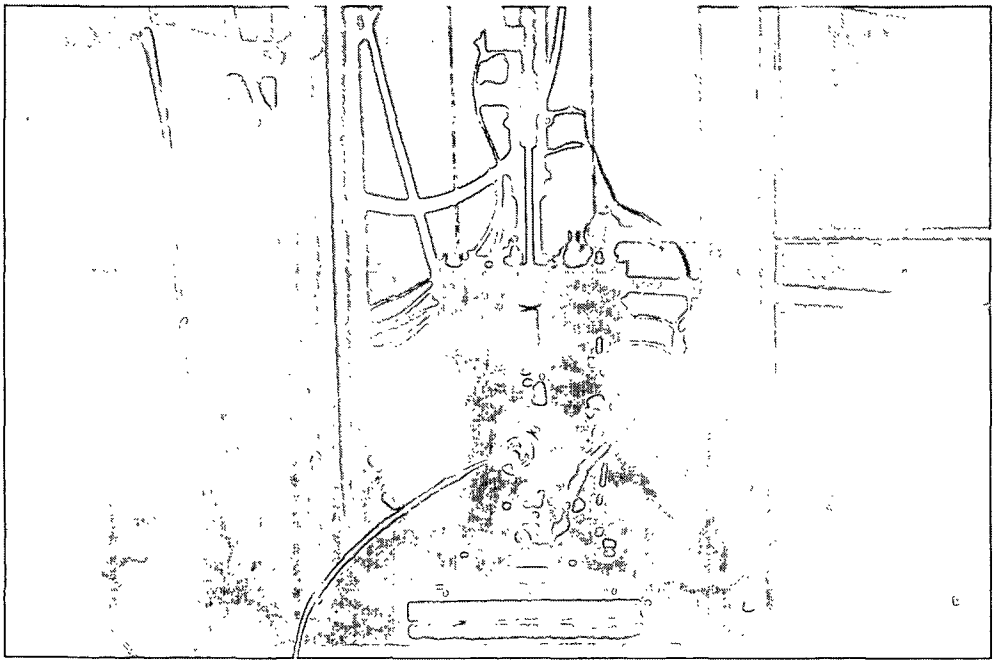

Figure 3. Slow strain rate test apparatus.

The 316 SS test specimen was electrically isolated from the grips by mica washers. A collar attached to the sample was connected to a post on the bottom of the autoclave. The post was electrically isolated from the autoclave but in electrical contact with the potentiostat which was used in the tests under controlled potential. An external silver-silver chloride reference electrode was used. This was calibrated versus a saturated calomel electrode prior to each new set of polarization measurements.

RESULTS AND DISCUSSION

POLARIZATION BEHAVIOR AT 90°C

Polarization curves were generated for 304 and 316 stainless steels in the test environments to identify differences in behavior. The curves are illustrated in Appendix A, Fig. A1-A4. No significant differences in behavior were observed in these straight sulfite solutions. The curves moved upward in potential as the pH is reduced. Most electrochemical reactions would be expected to move to higher potential as pH decreases.

The corrosion potential (E_{corr}) rests in the passive range and the alloys had approximately the same E_{corr}. At pH 7 and 1.5, the 304 had a higher potential than the 316 SS. The corrosion potential appears to be controlled by the hydrogen reduction reaction. In the higher pH solutions containing chloride, the corrosion potentials were significantly higher than observed in solutions without chloride, suggesting that corrosion potential is not controlled by the cathodic hydrogen evolution reaction.

Effect of Sodium Chloride Additions

Polarization curves for 304 and 316 stainless steels in the straight sulfite solutions with additions of 1 g/L NaCl are illustrated in Appendix A, Fig. A5-A9. Higher polarization currents were observed on 304 SS at potentials just above the corrosion potential indicating that the passive film might be less protective. Otherwise, the behavior of 304 and 316 was similar. Pitting and crevice corrosion was observed on the electrodes after scanning. Pitting scans would have been more appropriate for this environment, to determine the breakdown potential for pitting.

Effect of Sodium Thiosulfate Additions

Additions of 5 g/L $Na_2S_2O_3$ were made to the sulfite solutions. Polarization curves for 304 and 316 stainless steels are illustrated in Appendix A, Fig. A10-A14. No significant differences were observed. Thus, thiosulfate at these concentrations does not appear to initiate any significant additional electrochemical reactions.

WEIGHT LOSS AND POTENTIAL MEASUREMENTS AT 90°C

Results of weight loss tests for sulfite solutions are summarized in Table 3. These test results formed a basis of comparison for the investigation of the effects of additives. In the cases where pH decreased significantly during the test, the corrosion rate was higher, especially in the vapor phase. Acidic condensation may have formed on the electrode in the vapor phase and dripped, with corrosion products, into the liquid phase. The decrease in pH during the test may have been due in part to hydrolysis of corrosion products. Metal ions in the liquor could then have catalyzed breakdown of the liquor. Slightly higher corrosion rates in the liquid phase did not seem to be caused by lower pH alone, otherwise corrosion rates would have been higher in the more acidic solutions. Interestingly, corrosion rates were slightly higher in the alkaline sulfite solutions than in the bisulfite and acid sulfites, which was unexpected. This difference appears to be related to the drop in pH during the test.

Results of potential monitoring during weight loss tests are illustrated in Appendix A, Fig. A15-A21. In the 8.5 g/L Na_2SO_3 solution, the pH fell significantly during the test for both steels, and higher corrosion rates were measured than in the 6 g/L Na_2SO_3 solution. At pH 7, the steels showed a similar drop in pH in the solution containing 16.5 g/L Na_2SO_3. The increasing potentials in these tests (Fig. A15, A16, A17) may have been due to the

Table 3. Corrosion rates in sulfite solutions.

Environment	Phase	Material	Corrosion rate, mpy	Initial pH	Final pH
6 g/L	liq.	304	< 0.1	10.1	7.8
Na_2SO_3	liq.	316	< 0.1		
pH 10	vap.	304	< 0.1		
	vap.	316	< 0.1		
8.5 g/L	liq.	304	0.12	10.2	3.8
Na_2SO_3	liq.	316	0.11		
pH 10	vap.	304	0.12		
	vap.	316	0.11		
16.5 g/L	liq.	304	< 0.1	7.4	2.6
Na_2SO_3	liq.	316	< 0.1		
pH 7	vap.	304	0.13		
	vap.	316	0.12		
59 g/L	liq.	304	0	7.2	6.7
Na_2SO_3	liq.	316	0		
pH 7	vap.	304	< 0.1		
	vap.	316	< 0.1		
26 g/L	liq.	304	< 0.1	4.2	4.0
$NaHSO_3$	liq.	316	0		
pH 4	vap.	304	0		
SO_2 addn.	vap.	316	0		
10 g/L	liq.	304	0	4.2	4.0
$NaHSO_3$	liq.	316	0		
pH 4	vap.	304	0		
SO_2 addn.	vap.	316	0		
52.5 g/L	liq.	304	0.1	N.A.	N.A.
$NaHSO_3$	liq.	316	0		
pH 1.5	vap.	304	0		
SO_2 addn.	vap.	316	0		

decreasing pH during the test. In the solution containing 59 g/L Na_2SO_3 (Fig. A18), the corrosion potential reached a steady value after 24 hours and remained there. The more concentrated solution apparently prevented a large decrease in pH. Corrosion potential was stable in the more acidic bisulfite solutions (pH 4) as illustrated in Fig. A19, with a lower potential in the more concentrated solution.

In a separate test, in alkaline sulfite liquor, one specimen was situated at the liquid/vapor interface. No enhancement of corrosion was observed at the interface. Perhaps this could be repeated in acid solutions in the presence of air to simulate the effect of air on acid condensates present on the surface. Experiments involving splashing of liquor onto the surface, described below, simulated an aspect of the liquid/vapor interface, but did not enhance corrosion rates.

Effect of Sodium Chloride Additions

Results of weight loss tests with additions of NaCl are listed in Table 4. Corrosion rates were low, even with this large concentration of NaCl (1 g/L). Higher rates of corrosion were observed at pH 4 with the addition of chloride, although the effect was small. Pitting was observed on the 304 stainless steel in the bisulfite solution. More pitting than this had been expected. After these tests it was concluded that some crevice type geometry would be necessary.

Results of potential monitoring during weight loss tests are illustrated in Appendix A, Fig. A22-A24. As seen in Fig. A22, the corrosion potential started at more noble values than in the chloride free solution (Fig. A16), and remained there throughout the test. At pH 7, the potential was very stable in the chloride solution, Fig. A23. At pH 4, Fig. A24, the potential was

stable at higher values than in solutions without chloride. Thus chloride tended to increase the measured corrosion potentials, as was observed also in the polarization study. If the potential increases sufficiently, then pitting can occur.

Table 4. Corrosion rates in solutions with NaCl additions.

Environment	Phase	Material	Corrosion rate, mpy
8.5 g/L	liq.	304	0
Na_2SO_3 +	liq.	316	< 0.1
1 g/L	vap.	304	0
NaCl	vap.	316	< 0.1
pH 10			
16.5 g/L	liq.	304	< 0.1
Na_2SO_3 +	liq.	316	< 0.1
1 g/L	vap.	304	< 0.1
NaCl	vap.	316	< 0.1
pH 7			
10 g/L	liq.	304	< 0.1
Na_2SO_3 +	liq.	316	< 0.1
1 g/L	vap.	304	0.7*
NaCl	vap.	316	< 0.1
pH 4			

* - Pitting was observed. A whitish chemical deposit was observed at the gasket area at the top of the sample.

In another series of tests, the electrodes were splashed with the sulfite solutions containing chloride additions once daily by vigorously shaking the test container. The objective was to form chloride deposits which might stimulate corrosion, or to simulate the process conditions more closely. Duplicate electrodes were exposed. One of these had a piece of string tied around it approximately at the midpoint along the length of the electrode to simulate the effect of a crevice under a deposit. A range of lower pH's was selected to stimulate acid condensation. The results of those tests are summarized in Table 5. Results were not significantly different than without

splashing. Perhaps splashing was too frequent, thereby rinsing off acidic condensates and crevice environments. On the other hand, the string should have acted as a crevice to retain a corrosive environment.

Table 5. Corrosion rates in solutions with chloride additions under splashing conditions.

Environment	Phase	Material	Corrosion rate, mpy
16.5 g/L	vap.	304	< 0.1
Na_2SO_3 +	vap./string	304	< 0.1
1 g/L NaCl	vap.	316	0.1
pH 7	vap./string	316	0.1
59 g/L	vap.	304	< 0.1
Na_2SO_3 +	vap./string	304	< 0.1
1 g/L NaCl	vap.	316	< 0.1
pH 7	vap./string	316	0.1
10 g/L	vap.	304	< 0.1
Na_2SO_3 +	vap./string	304	0
1 g/L NaCl	vap.	316	0
pH 4	vap./string	316	0
26 g/L	vap.	304	< 0.1
Na_2SO_3 +	vap./string	304	-
1 g/L NaCl	vap.	316	< 0.1
pH 4	vap./string	316	-
52.5 g/L	vap.	304	< 0.1
Na_2SO_3 +	vap./string	304	-
1 g/L NaCl	vap.	316	-
pH 1.5	vap./string	316	0

(-) - weight gain

Effect of Thiosulfate Additions

Results of weight loss tests with thiosulfate are listed in Table 6. Severe corrosion of 304 SS in the vapor phase of the pH 4 environment was observed in the first run, but could not be duplicated in a second test. Corrosion products from the vapor phase 304 SS electrode coated the 304 in the

liquid phase, and the deposit could not be removed chemically. The 316 SS in the liquid was not stained. These results indicate the potential for severe corrosion in the presence of thiosulfate.

Table 6. Corrosion rates in solutions with additions of thiosulfate.

Environment	Phase	Material	Corrosion rate, mpy
8.5 g/L	liq.	304	< 0.1
Na_2SO_3 +	liq.	316	< 0.1
5 g/L $Na_2S_2O_3$	vap.	304	0
pH 10	vap.	316	< 0.1
16.5 g/L	liq.	304	< 0.1
Na_2SO_3 +	liq.	316	< 0.1
5 g/L $Na_2S_2O_3$	vap.	304	< 0.1
pH 7	vap.	316	< 0.1
10 g/L	liq.	304	0
Na_2SO_3 +	liq.	316	0.1
5 g/L $Na_2S_2O_3$	vap.	304	21.5/0
pH 4	vap.	316	< 0.1

Results of potential monitoring during weight loss tests are illustrated in Appendix A, Fig. A25-A27. In the bisulfite solution at pH 4 there was a large difference between the 304 and 316 stainless steels.

Attempts to condense acid on a cold finger were unsuccessful. Perhaps the temperature was too low and caused excess condensation. Further efforts should be made to analyze thiosulfate concentrations following tests because thiosulfate may have catalyzed the liquor breakdown. Metal ions dripping into the solution will also catalyze liquor breakdown.

A splash test was done in 10 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$ at pH 4 to determine whether the surface could be activated by contamination with thiosulfate. The results are summarized in Table 7. No significant corrosion

was detected. Splashing may have washed away the corrosive environment, although this seems unlikely under the string.

Table 7. Corrosion rates in solutions with thiosulfate additions under splashing conditions.

Environment	Phase	Material	Corrosion rate, mpy
10 g/L	vap.	304	0
Na_2SO_3 +	vap./string	304	0
5 g/L $Na_2S_2O_3$	vap.	316	0
pH 4	vap./string	316	< 0.1

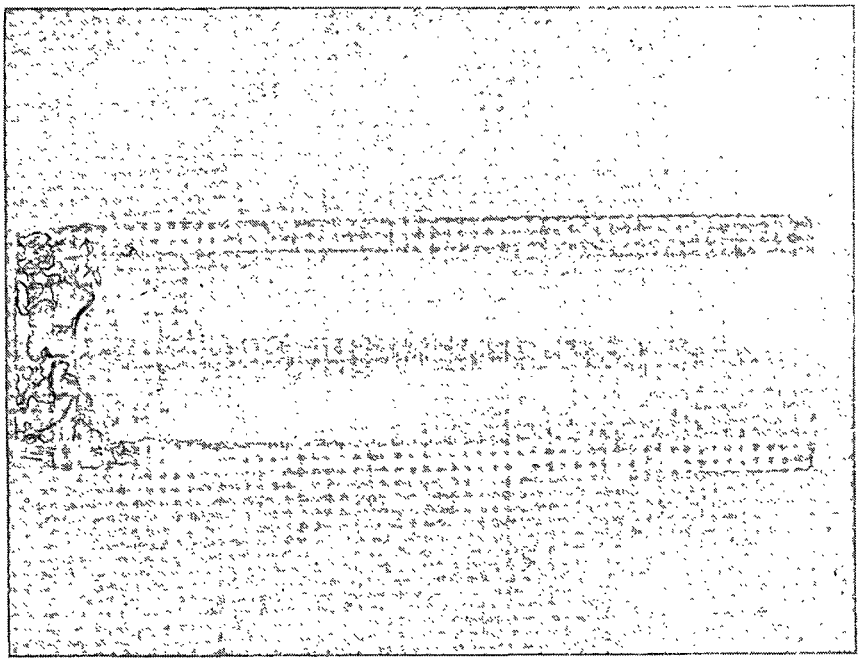

Figure 4. Pitting occurred at the gasket in the bisulfite solution at pH 4.

Effect of Air

Results of weight loss tests with the solutions exposed to air are listed in Table 8. In general, there was no more corrosion than in the tests with a nitrogen atmosphere in the cell. This was surprising because air is known to stimulate formation of acidic condensates in mechanical pulping systems.

Table 8. Corrosion rates in the sulfite solutions exposed to air.

Environment	Phase	Material	Corrosion rate, mpy
6 g/L	liq.	304	0.14
Na_2SO_3	liq.	316	0.03
pH 10	vap.	304	0.09
	vap.	316	0.08
8.5 g/L	liq.	304	0.05
Na_2SO_3	liq.	316	0.05
pH 10	vap.	304	0.1
	vap.	316	0.04
16.5 g/L	liq.	304	0.07
Na_2SO_3	liq.	316	0
pH 7	vap.	304	0.06
	vap.	316	0.06
59 g/L	liq.	304	0
Na_2SO_3	liq.	316	0.02
pH 7	vap.	304	0.11
	vap.	316	0.02
10 g/L	liq.	304	0.03
Na_2SO_3	liq.	316	0.05
pH 4	vap.	304	0
	vap.	316	0.16
26 g/L	liq.	304	0
Na_2SO_3	liq.	316	0.11
pH 4	vap.	304	0
	vap.	316	0.14
52.5 g/L	liq.	304	0
Na_2SO_3	liq.	316	0
pH 1.5	vap.	304	0.01
	vap.	316	0.11

Results of potential monitoring during weight loss tests are plotted in Appendix A, Fig. A29-A34. To see the effect of exposure to air, these figures should be compared with Fig. A15-A21. At pH 10, 7, and 1.5 the starting corrosion potential was higher in the solutions exposed to air. At pH 4, the behavior was very similar. There was little difference between the two stainless alloys in the solutions exposed to air.

Vapor phase testing did not simulate what happens in the mill. Perhaps the temperature was not low enough for sufficient condensation to occur. A probe cooled to enhance condensation may be necessary. Some new method for vapor phase testing is needed.

POLARIZATION BEHAVIOR AT 150°C

Polarization curves were generated for 304 and 316 stainless steels at 150°C, and are illustrated in Appendix B, Fig. B1-B7. Anodic currents were slightly higher than at 90°C, as would be expected. At pH 4 (Fig. B5 and B6), the steels did not have the same E_{corr} at 150°C as at 90°C. The E_{corr} was lower at pH 1.5. Otherwise, the behavior was relatively similar.

Effect of Sodium Chloride Additions

The effects of NaCl additions on polarization curves are illustrated in Appendix B, Fig. B8-B12. There were no significant differences between the 316 and 304 alloys. There were some differences compared to the curves at 90°C. At pH 7 in the 65 g/L sulfite solution, (Fig. B10 and A7), the currents were much higher at 150°C, with no passive range observed. This was also true for the pH 4, 12 g/L and 30 g/L solutions (Fig. B11 and A8; B12 and A9). Thus the chloride was much more damaging to the passivity at 150°C, and may have a greater effect under refiner conditions. These results indicate that additional

study of the effects of chloride at high temperature may turn up significant corrosion problems.

Effect of Sodium Thiosulfate Additions

The effects of $Na_2S_2O_3$ additions on polarization behavior are illustrated in Appendix B, Fig. B13-B17. There was no significant difference in behavior between the alloys to suggest that corrosive effects might be worse at the higher temperature. The behavior was very close to that found at 90°C. At pH 4, however, the E_{corr} was higher and currents were more erratic (Fig. B17 versus A14). In a pitting scan at 150°C for 304 stainless steel, pitting was indicated (Fig. B17).

WEIGHT LOSS AND POTENTIAL MONITORING AT 150°C

Results of weight loss tests for sulfite solutions are summarized in Table 9. Corrosion rates were as low as at 90°C. These results indicate that no significant increases would be expected in the liquid phase at the higher temperatures in the straight sulfite solutions. The effects of additives were not examined. In the 15 g/L Na_2SO_3 solution at pH 7, there was a light grey film with a speckled appearance formed on the coupon in the liquid phase. The film was fairly adherent. Results of potential monitoring during weight loss tests are illustrated in Fig. B18-B21.

STRESS CORROSION CRACKING SUSCEPTIBILITY AT 150°C

In the straight sulfite test solutions, the 316 stainless steel did not suffer stress corrosion cracking at the corrosion potential. Load-elongation curves for the slow strain rate tests of 316 SS at pH 4-10 are illustrated in Fig. 5. These results show that the specimens failed in normal ductile fashion, and that stress corrosion cracking did not occur. Results are summarized in

Table 10. The percent reduction in diameter was high for all of the specimens, indicating that they 'necked down' and failed in a ductile manner.

Table 9. Corrosion rates in sulfite solutions at 150°C.

Environment	Phase	Material	Corrosion rate, mpy
8.5 g/L	liq.	304	0
Na_2SO_3	liq.	316	< 0.1
pH 10	vap.	304	< 0.1
	vap.	316	0.1
16.5 g/L	liq.	304	0.1
Na_2SO_3	liq.	316	< 0.1
pH 7	vap.	304	0
	vap.	316	0
59 g/L	liq.	304	0
Na_2SO_3	liq.	316	< 0.1
pH 7	vap.	304	-
	vap.	316	-

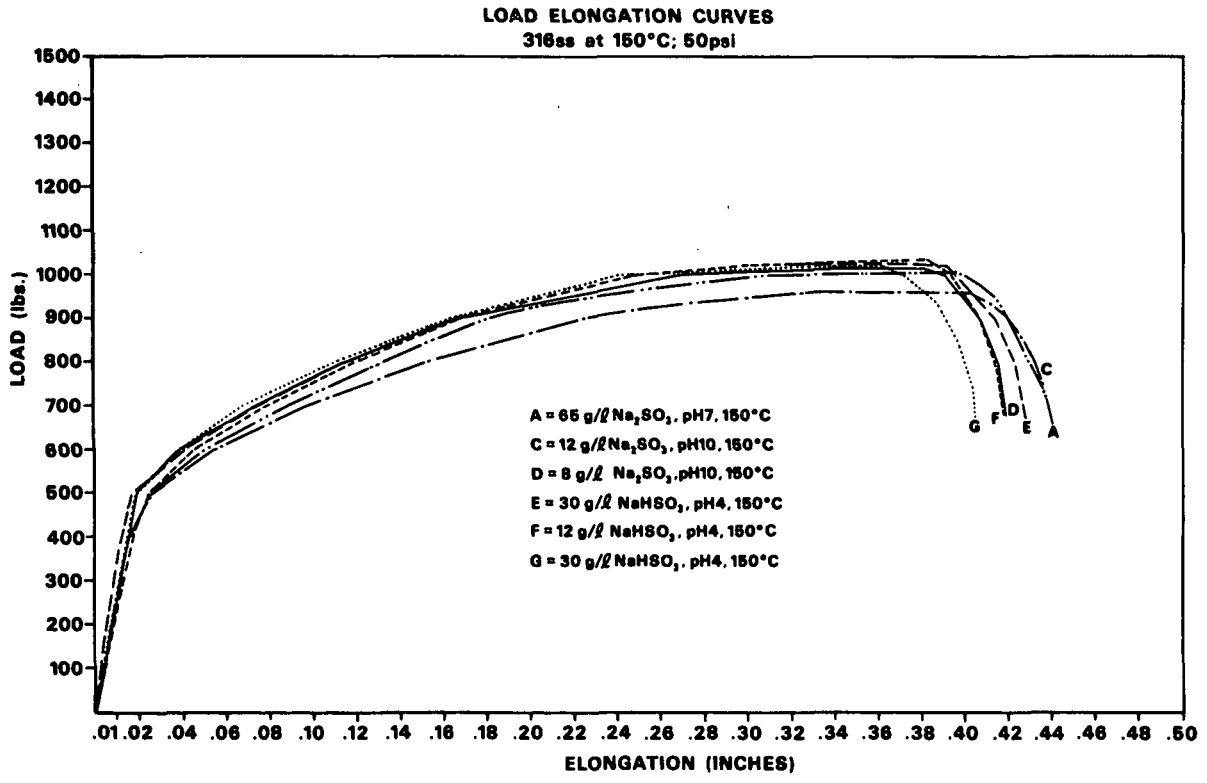

Figure 5. Load-elongation curves for 316 stainless steel in the straight sulfite solutions.

CONCLUSIONS

1. Base information has been obtained concerning corrosion in sulfite solutions representative of mechanical pulping environments. These data may be used for comparisons in investigation of the effects of additives or impurities in the processes.

2. Corrosion was more likely if pH < 7.

3. Additions of NaCl did not cause severe corrosion or pitting, although the test method may have been an inadequate simulation of the complex environment in a steaming tube or refiner. There was some evidence that chloride may potentially accelerate corrosion at 150°C.

4. Thiosulfate is potentially very harmful in mechanical pulping environments, judging by the severe pitting obtained in one test.

5. Air did not stimulate corrosive conditions significantly in these tests, although it is known to increase corrosion in pulp mills. Splashing the vapor phase test coupons to form corrosive deposits did not induce corrosion.

6. Insufficient data were obtained regarding stress corrosion cracking susceptibility. Further testing is required, especially to determine the conditions for chloride stress corrosion cracking.

7. Improved test methods must be devised to simulate vapor phase corrosion conditions in mechanical pulping systems.

8. This project was undertaken to provide base information for definition of a broader project to address problems which have been observed in mills. Difficulties of simulating those mill problems in controlled corrosion tests present obstacles to further research; means to overcome these obstacles must be identified before a broader project can be proposed.

SUGGESTIONS FOR FURTHER WORK

1. Use a higher Na_2SO_3 concentration than 30 g/L at pH 4 which would be closer to some process chemistries, and which may increase the chance of acid formation.

2. Devote more attention to pitting scans and measurement of pitting susceptibility in the presence of additions or impurities.

3. Use a cooled probe in an effort to condense vapors and acids on the test sample. Temperature of the probe would have to be optimized. If it is too low, excessive condensation will wash off acidic condensate.

4. Investigate other additions present as impurities or additives including $Al_2(SO_4)_3$, formic and acetic acid, lignosulfonates, $Na_2S_2O_4$ and H_2O_2. Tests of additives should include pH 1.5 environment as a simulation of acid condensation environments.

5. Study susceptibility to stress corrosion cracking at 150°C in the presence of air and with imposed potentials to simulate a range of possible conditions. A series of tests with chloride and thiosulfate additions should be conducted.

6. For the most aggressive environments rank alternative materials which may be employed to solve a specific problem.

ACKNOWLEDGMENT

Although the author (DCC) was the project leader, this project would not have been possible without the expert technical assistance of Mr. Mike Heath. Helpful discussions with S. K. Murarka and C. Reid are also acknowledged.

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THE INSTITUTE OF PAPER CHEMISTRY

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APPENDIX A

POLARIZATION BEHAVIOR AND POTENTIAL DECAY AT 90°C

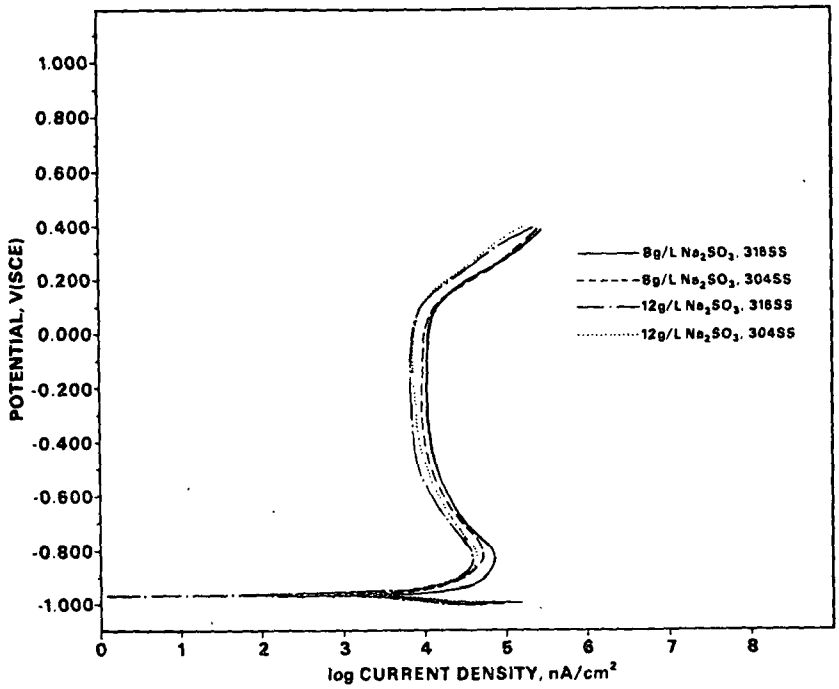

Figure A1. Polarization behavior of 304 and 316 stainless steels. 6 and 8.5 g/L Na_2SO_3, pH 10, 90°C.

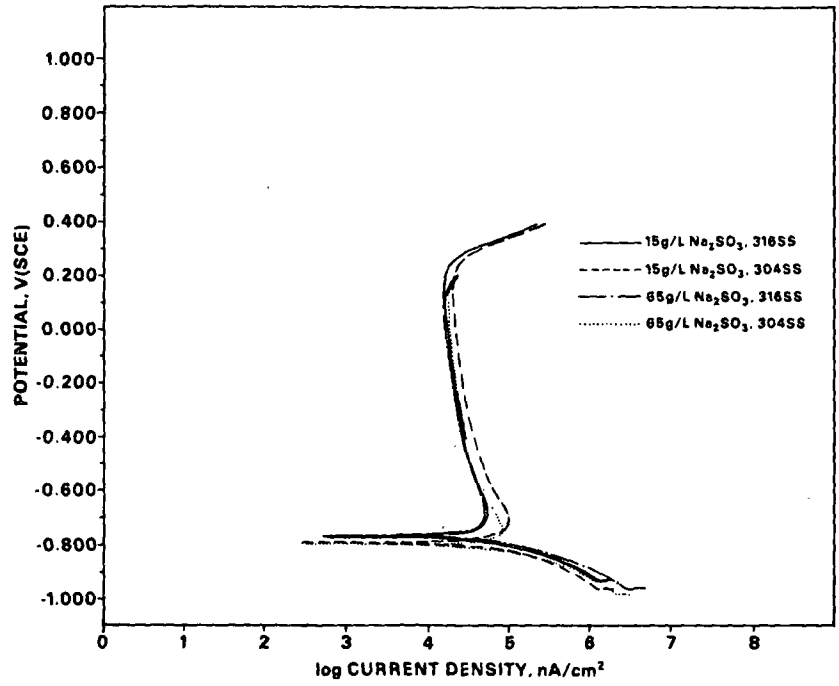

Figure A2. Polarization behavior of 304 and 316 stainless steels. 16.5 and 59 g/L Na_2SO_3, pH 7, 90°C.

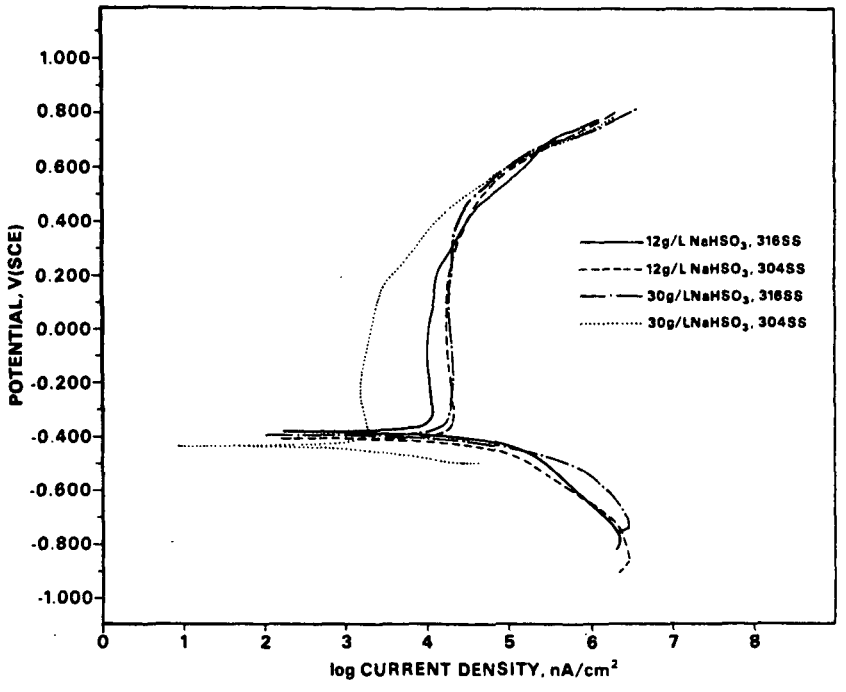

Figure A3. Polarization behavior of 304 and 316 stainless steels. 10 and 26 g/L $NaHSO_3$, pH 4, 90°C.

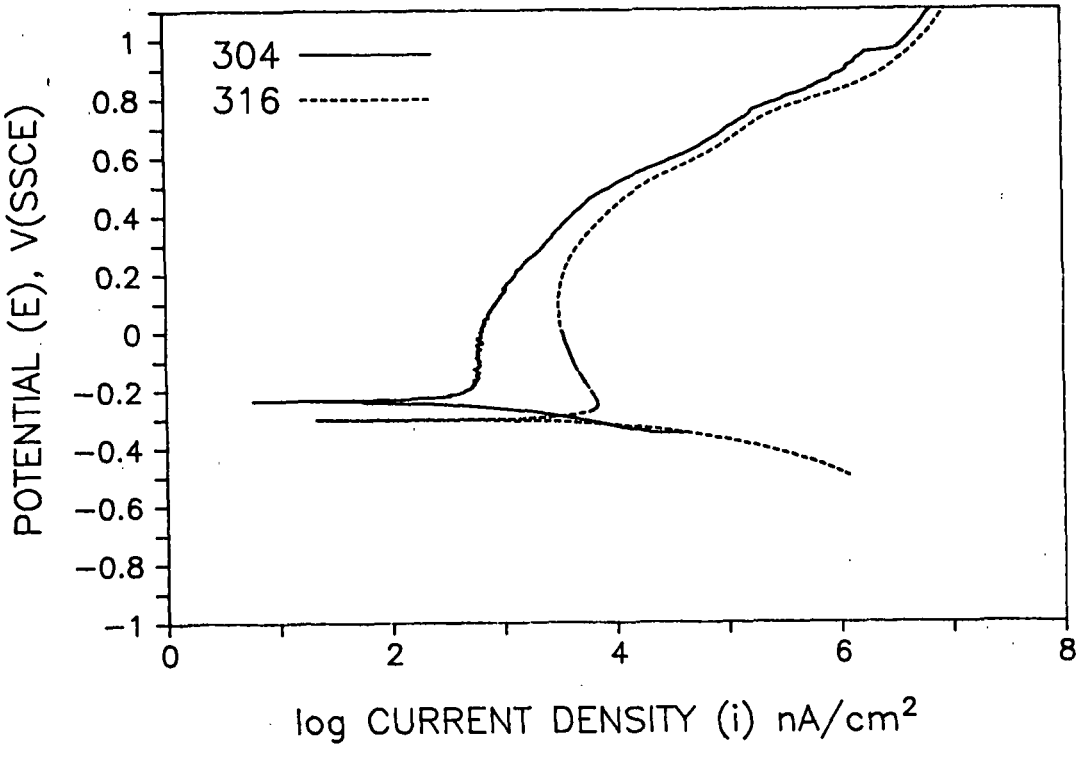

Figure A4. Polarization behavior of 304 and 316 stainless steels. 52.5 g/L $NaHSO_3$, pH 1.5, 90°C.

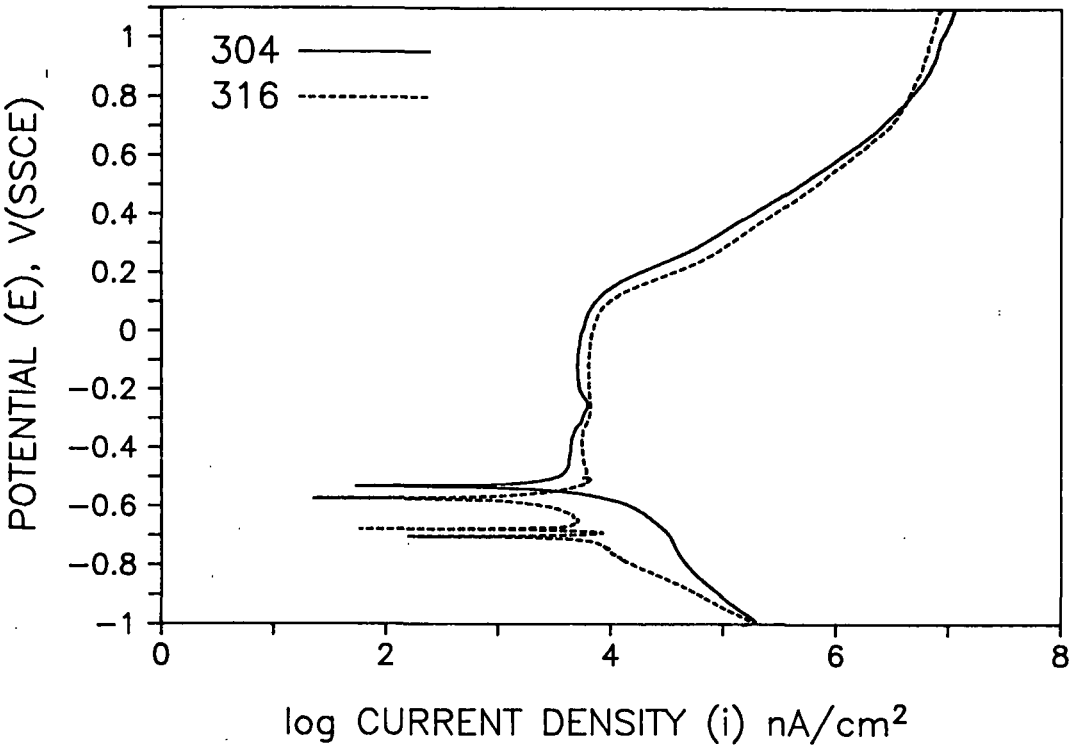

Figure A5. Polarization behavior of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3 + 1 g/L NaCl, pH 10, 90°C.

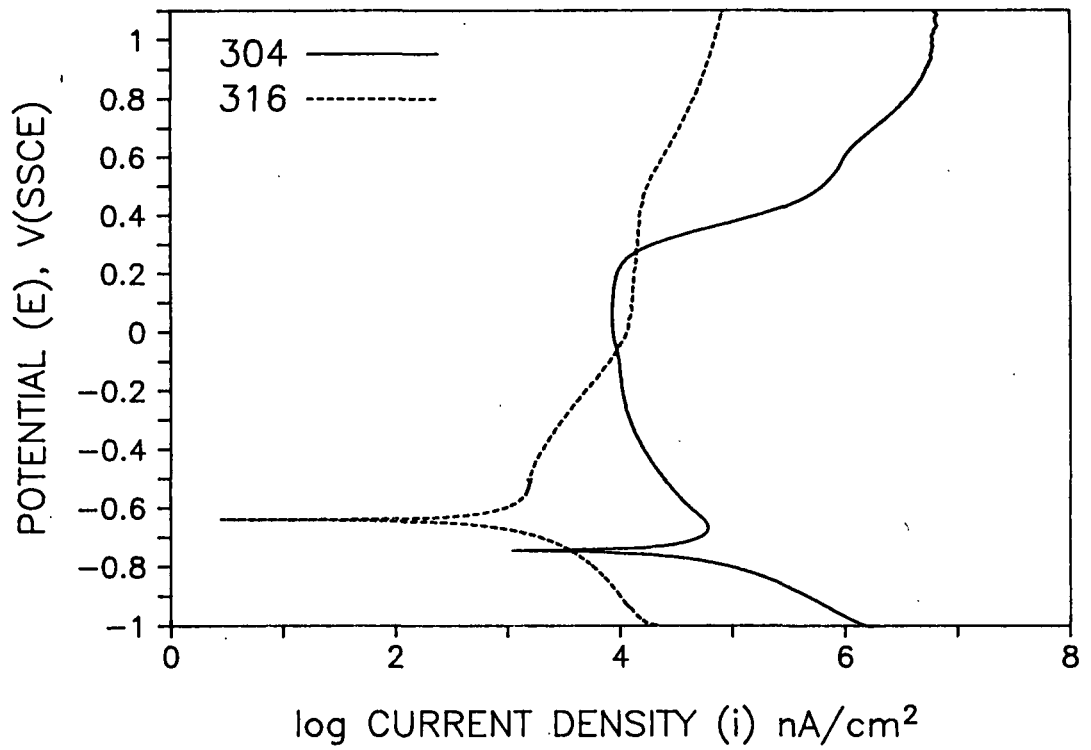

Figure A6. Polarization behavior of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3 + 1 g/L NaCl, pH 7, 90°C.

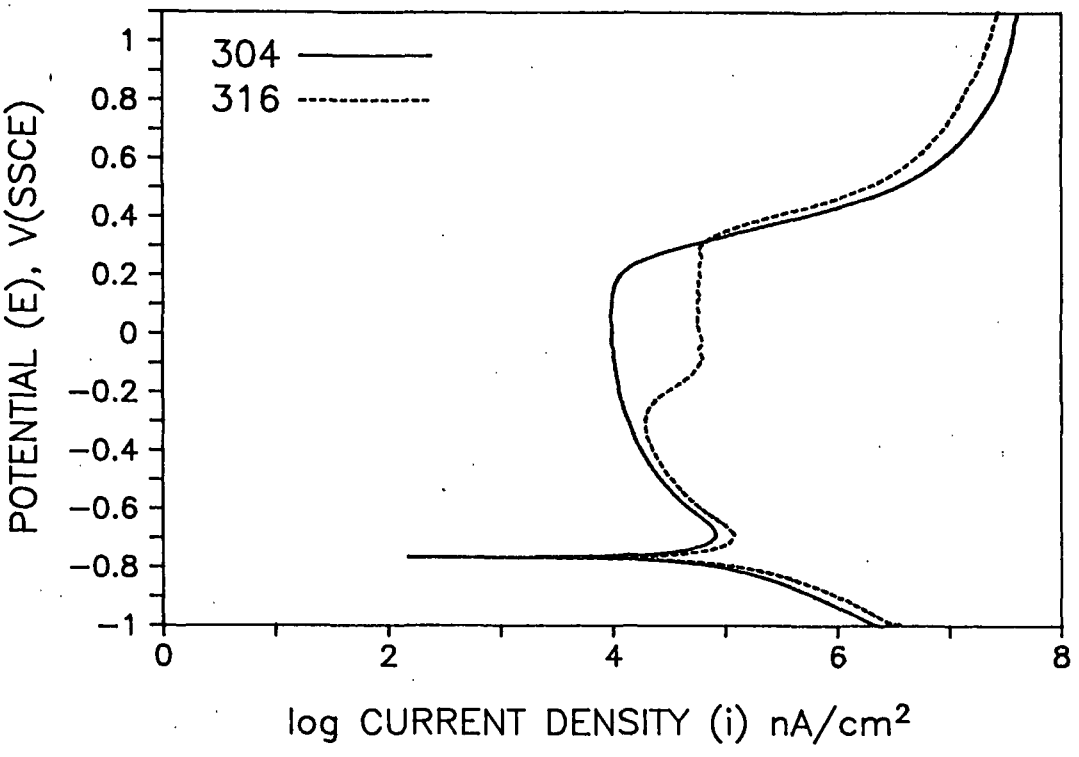

Figure A7. Polarization behavior of 304 and 316 stainless steels. 59 g/L Na_2SO_3 + 1 g/L NaCl, pH 7, 90°C.

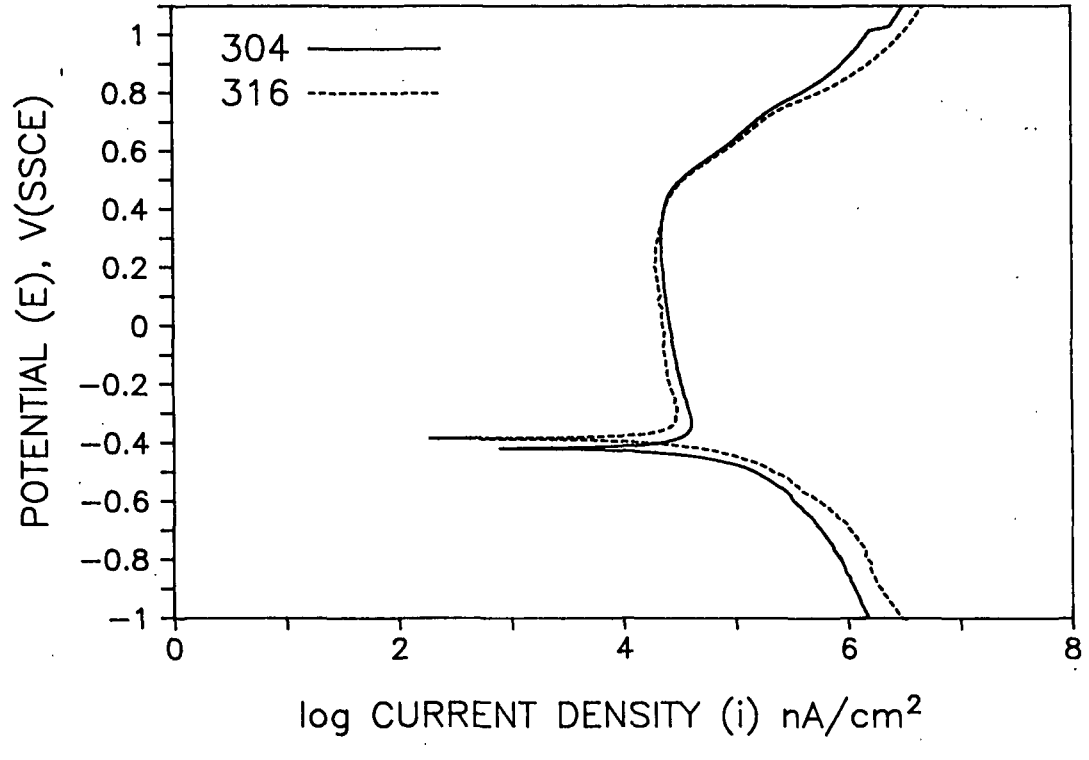

Figure A8. Polarization behavior of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 1 g/L NaCl, pH 4, 90°C.

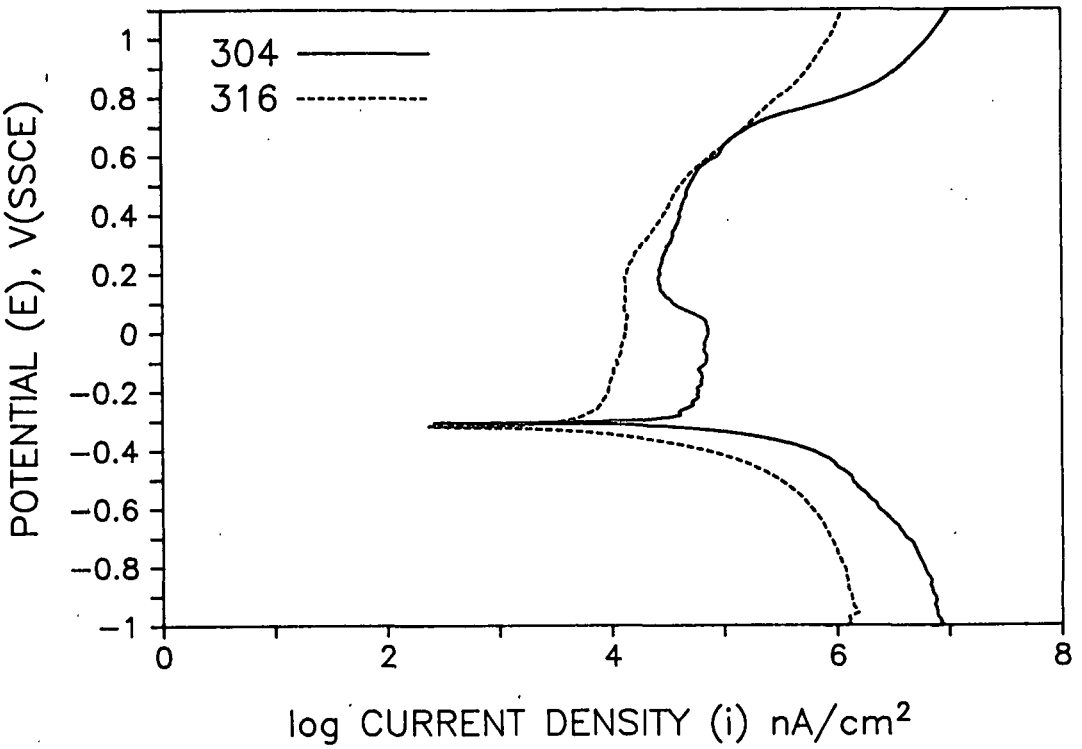

Figure A9. Polarization behavior of 304 and 316 stainless steels. 26 g/L Na_2SO_3 + 1 g/L NaCl, pH 4, 90°C.

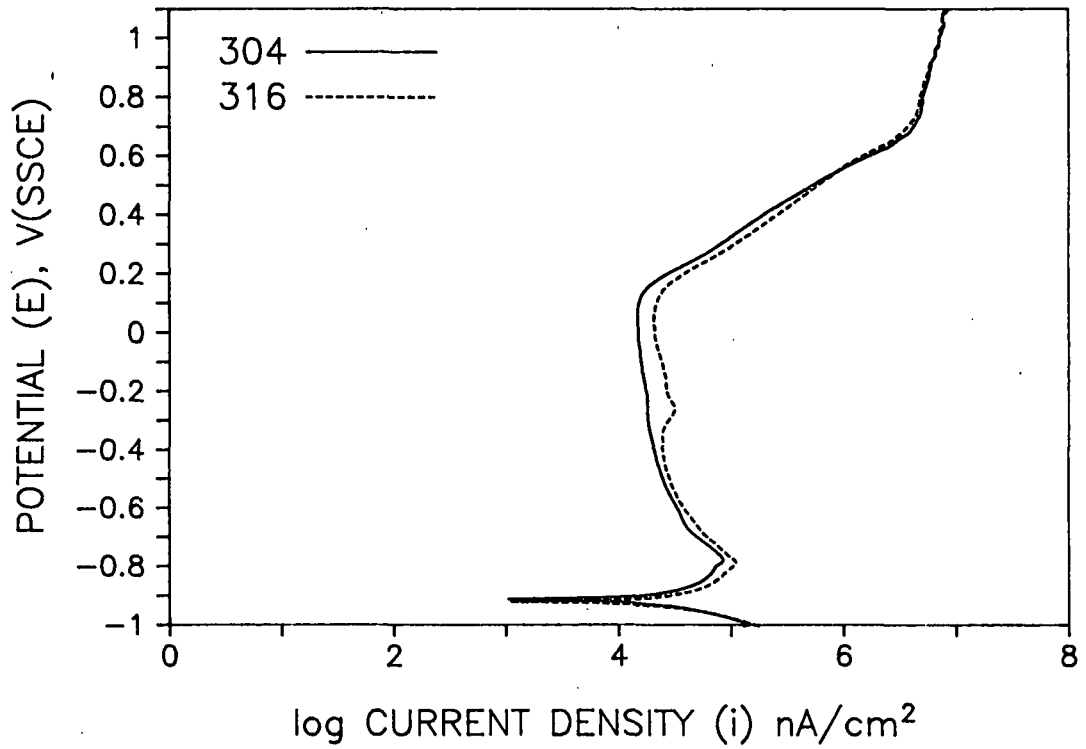

Figure A10. Polarization behavior of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 10, 90°C.

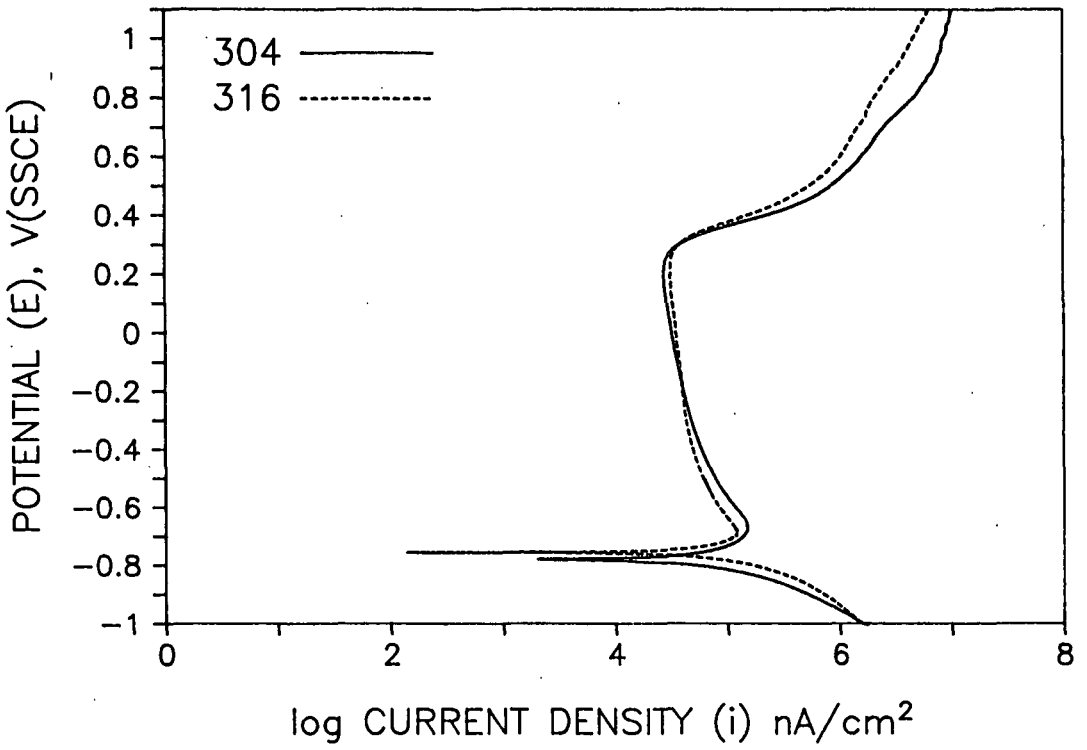

Figure A11. Polarization behavior of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 7, 90°C.

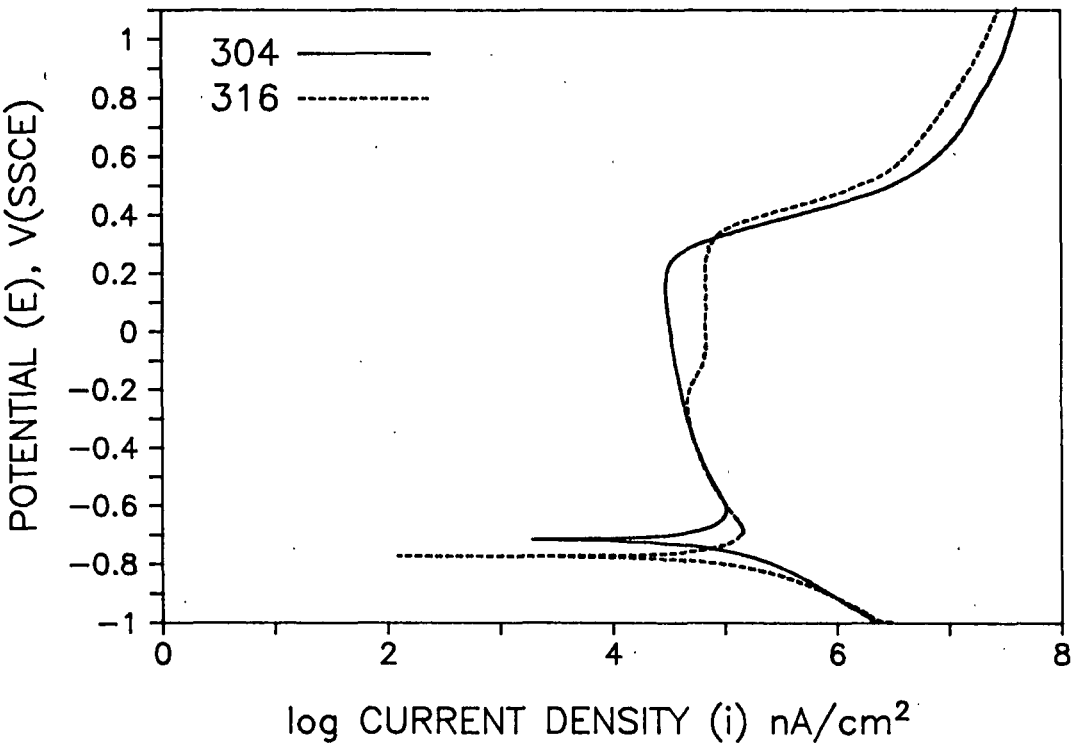

Figure A12. Polarization behavior of 304 and 316 stainless steels. 59 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 7, 90°C.

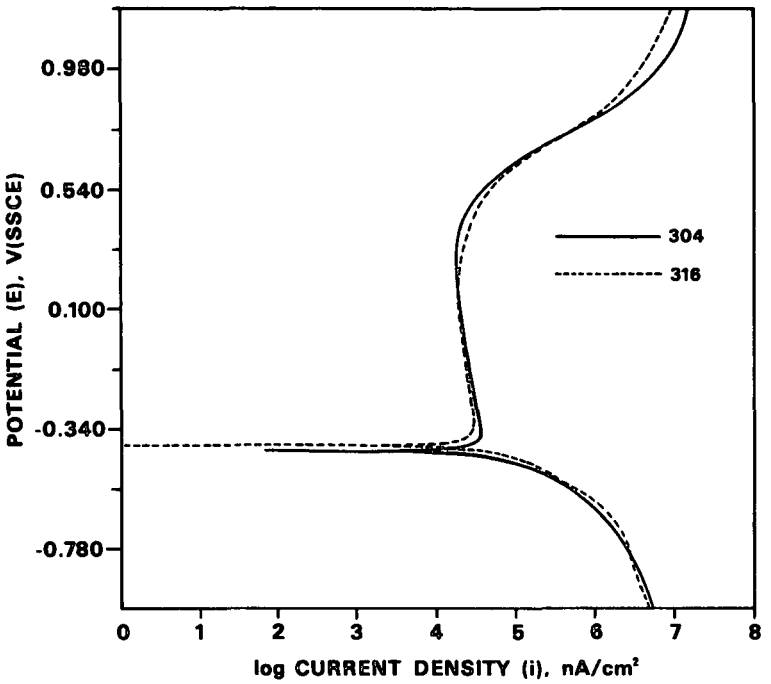

Figure A13. Polarization behavior of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 4, 90°C.

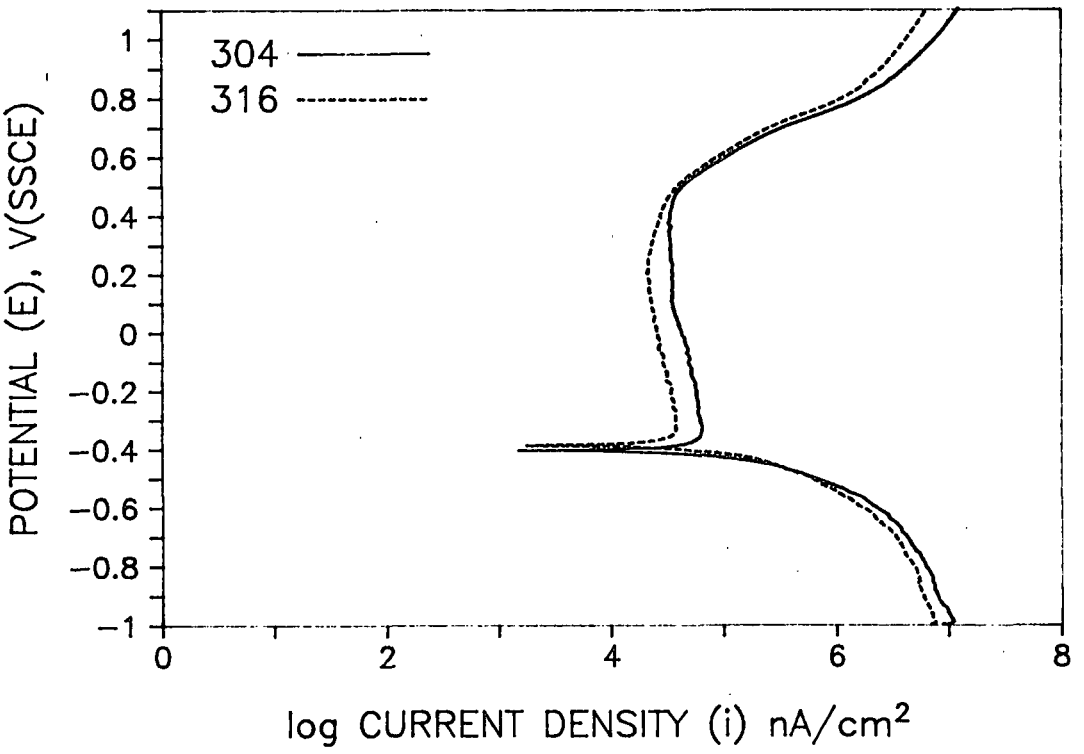

Figure A14. Polarization behavior of 304 and 316 stainless steels. 26 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 4, 90°C.

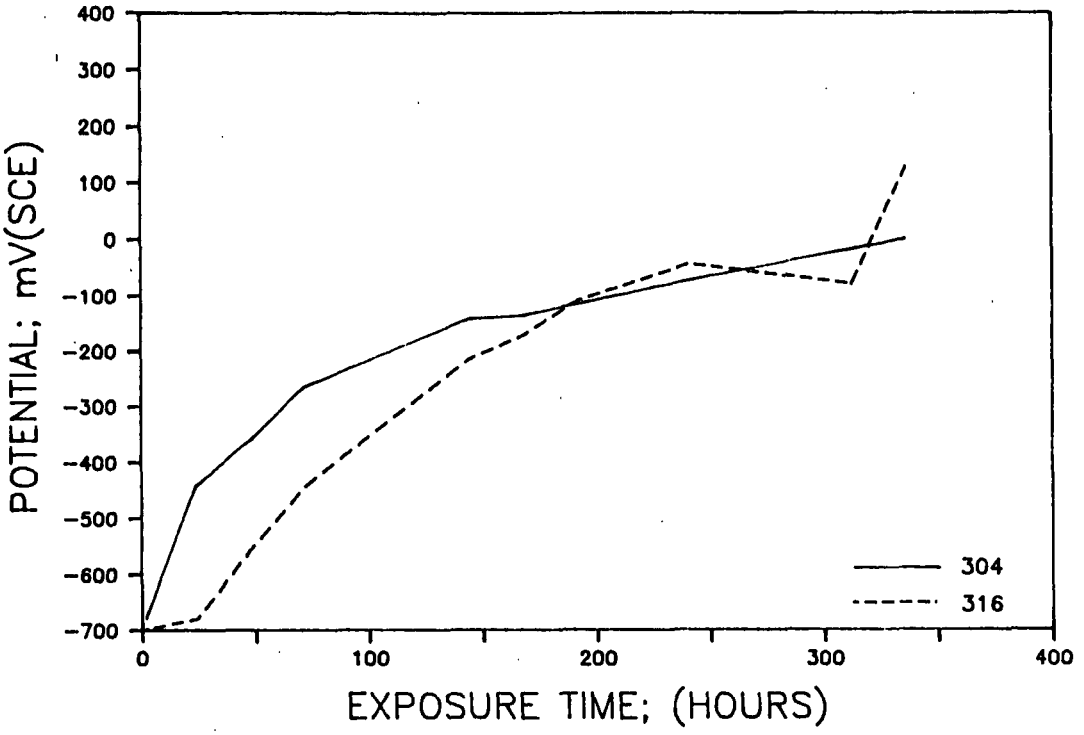

Figure A15. Corrosion potential versus time of 304 and 316 stainless steels. 6 g/L Na_2SO_3, pH 10, 90°C.

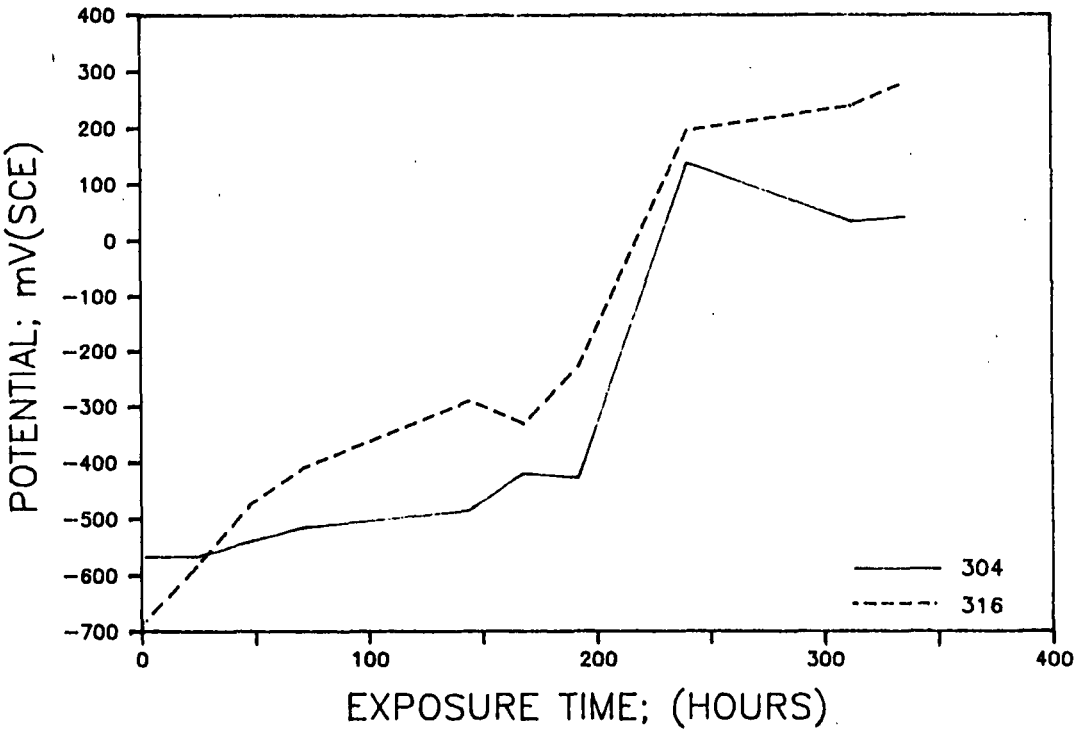

Figure A16. Corrosion potential versus time of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3, pH 10, 90°C.

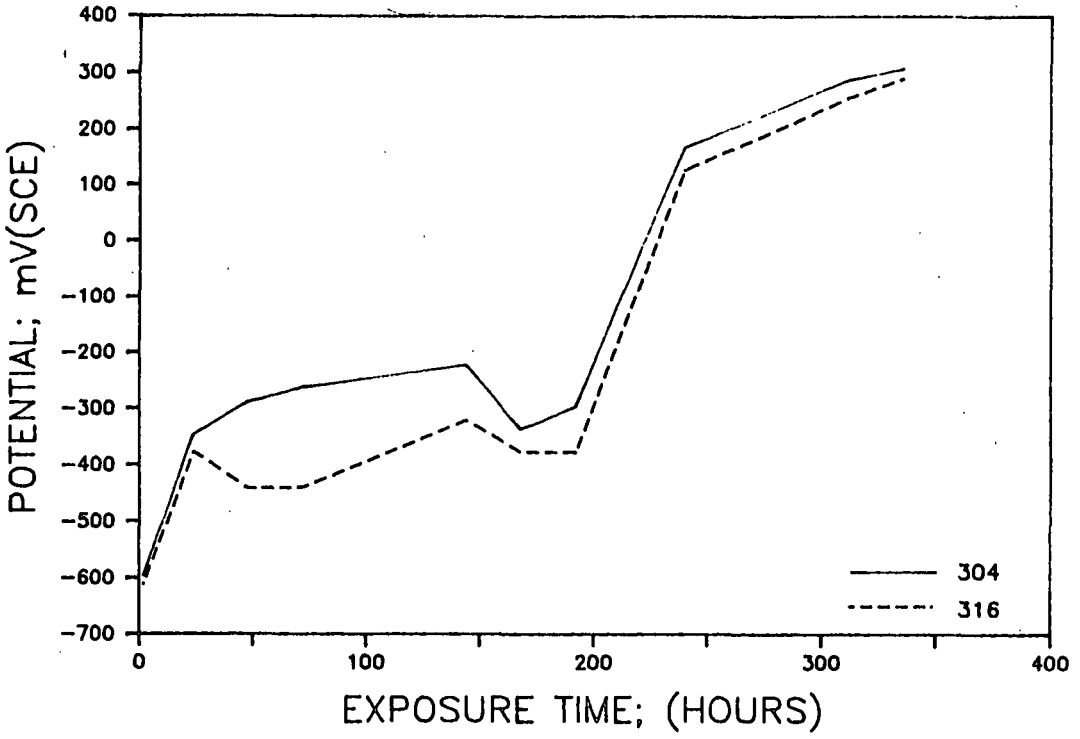

Figure A17. Corrosion potential versus time of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3, pH 7, 90°C.

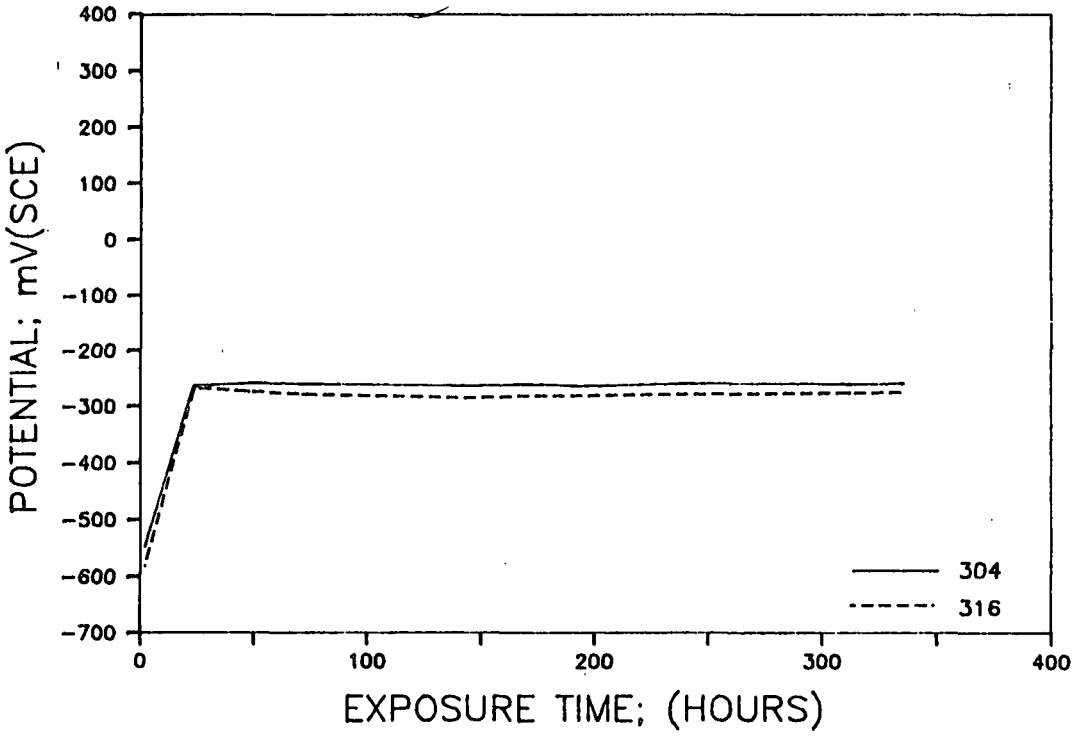

Figure A18. Corrosion potential versus time of 304 and 316 stainless steels. 59 g/L Na_2SO_3, pH 7, 90°C.

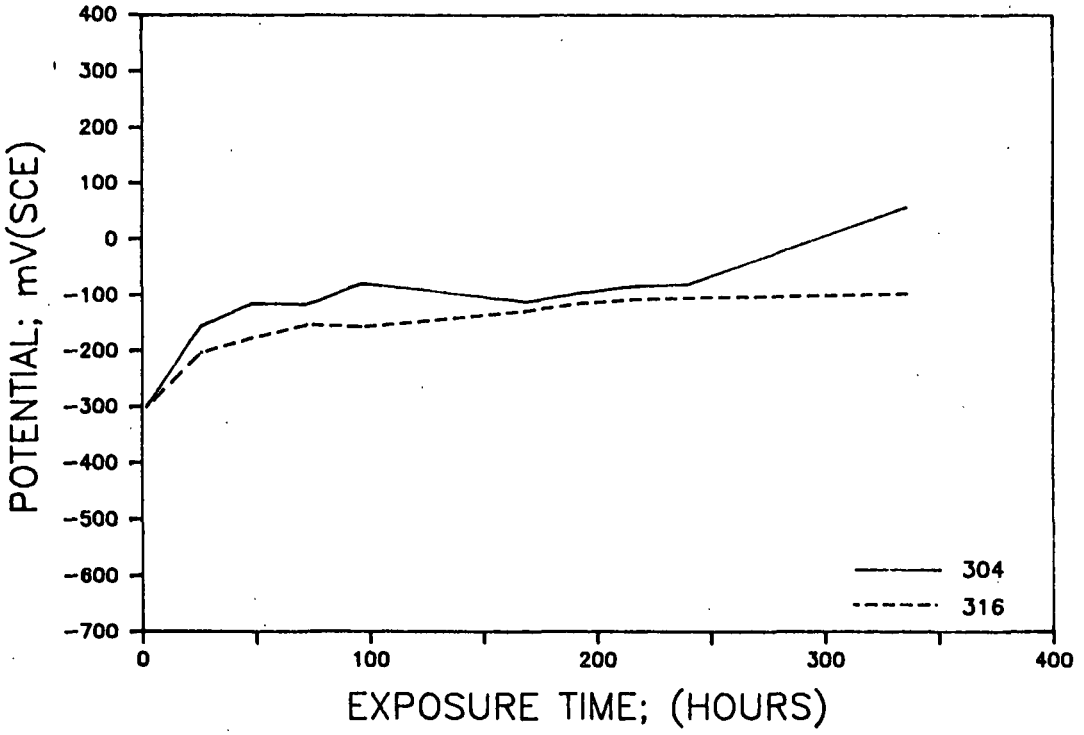

Figure A19. Corrosion potential versus time of 304 and 316 stainless steels. 10 g/L Na_2SO_3, pH 4, 90°C.

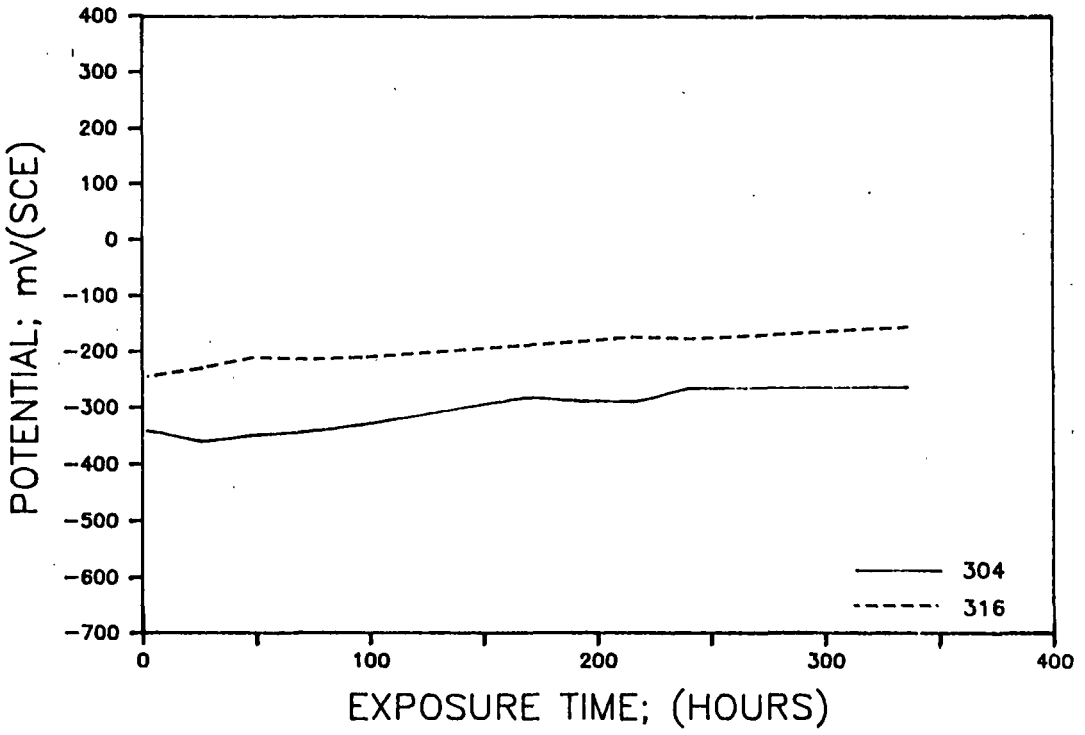

Figure A20. Corrosion potential versus time of 304 and 316 stainless steels. 26 g/L Na_2SO_3, pH 4, 90°C.

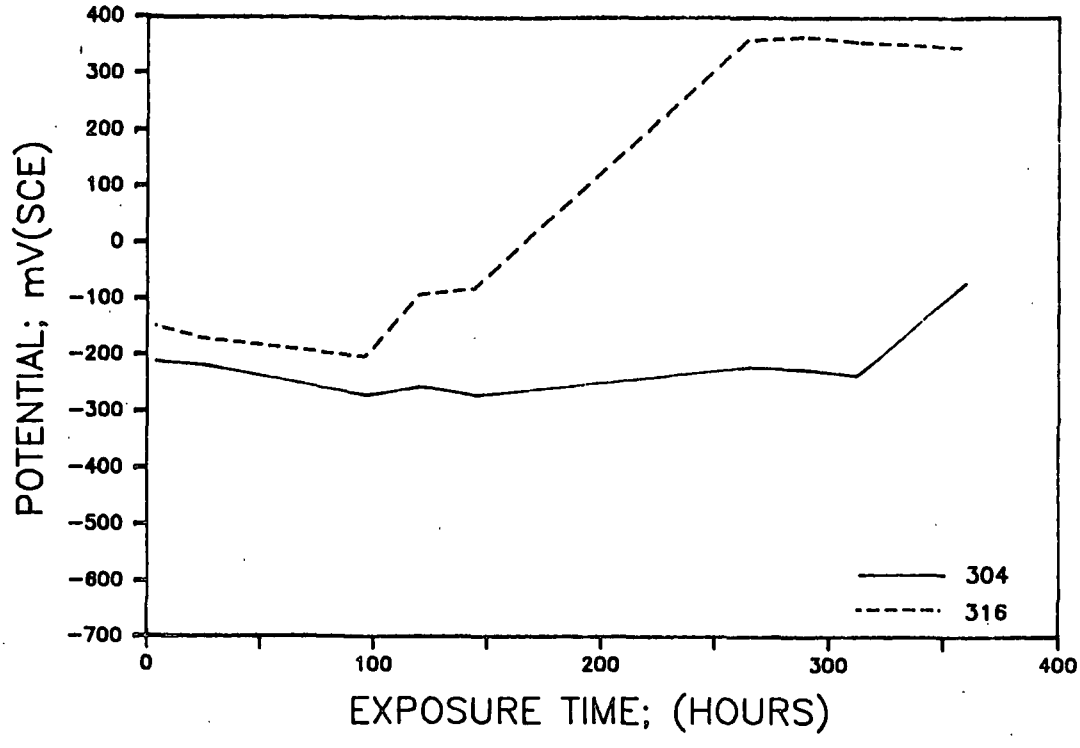

Figure A21. Corrosion potential versus time of 304 and 316 stainless steels. 52.5 g/L Na_2SO_3, pH 1.5, 90°C.

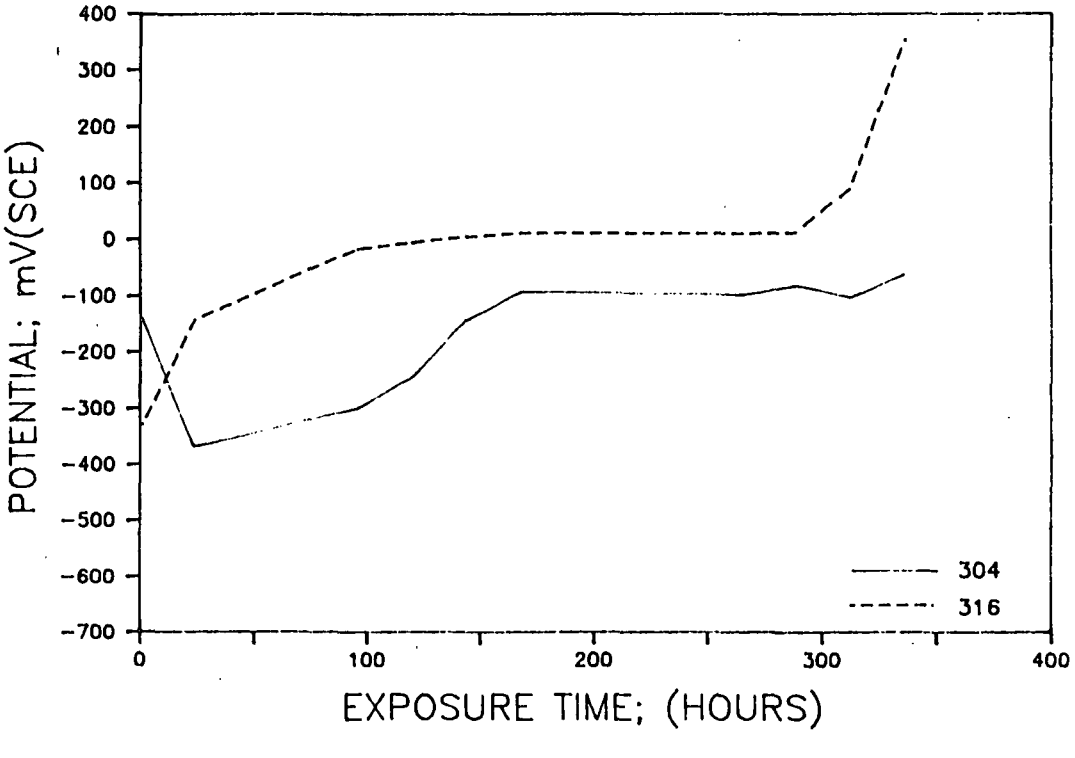

Figure A22. Corrosion potential versus time of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3 + 1 g/L NaCl, pH 10, 90°C.

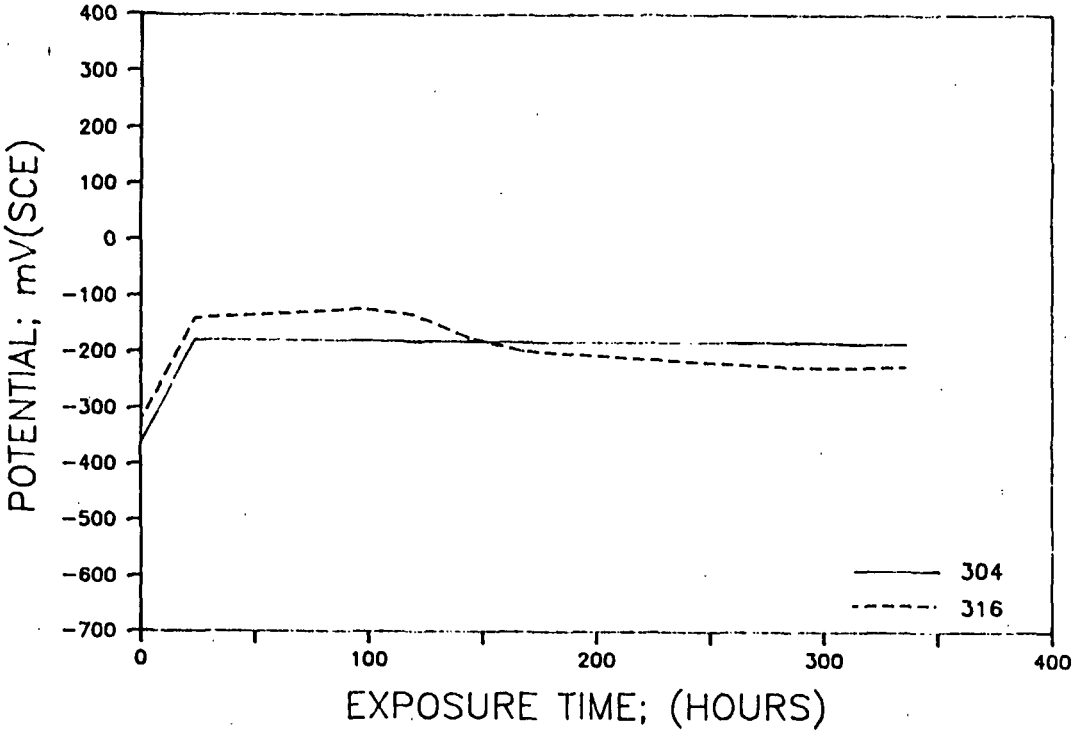

Figure A23. Corrosion potential versus time of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3 + 1 g/L NaCl, pH 7, 90°C.

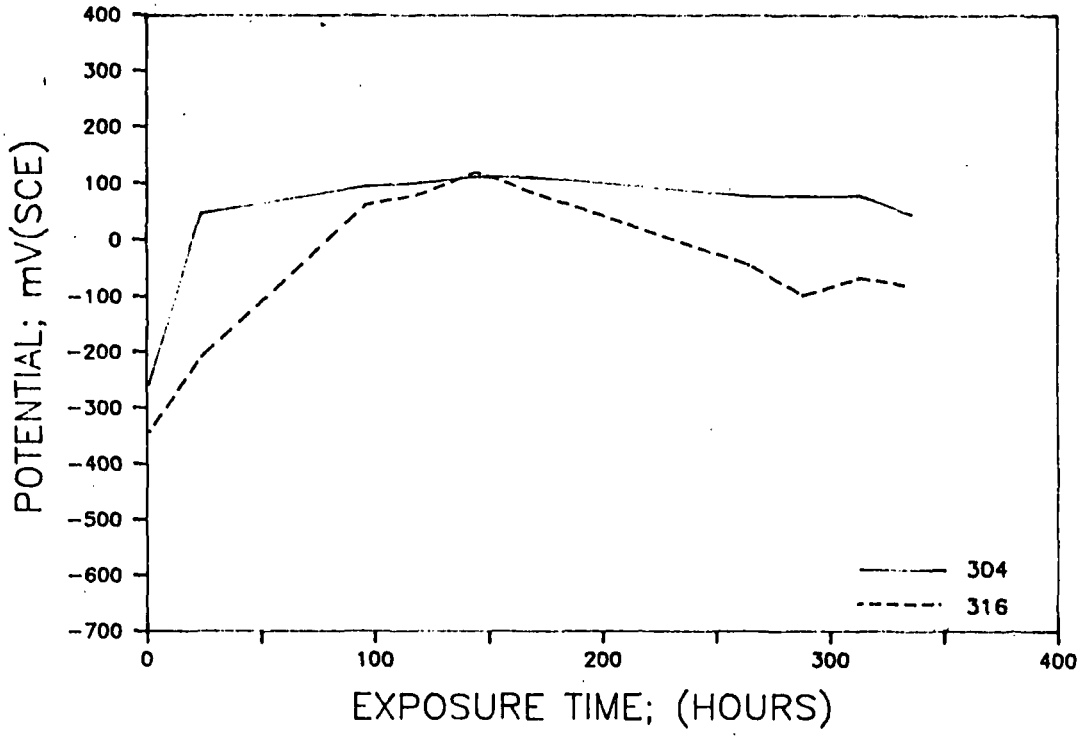

Figure A24. Corrosion potential versus time of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 1 g/L NaCl, pH 4, 90°C.

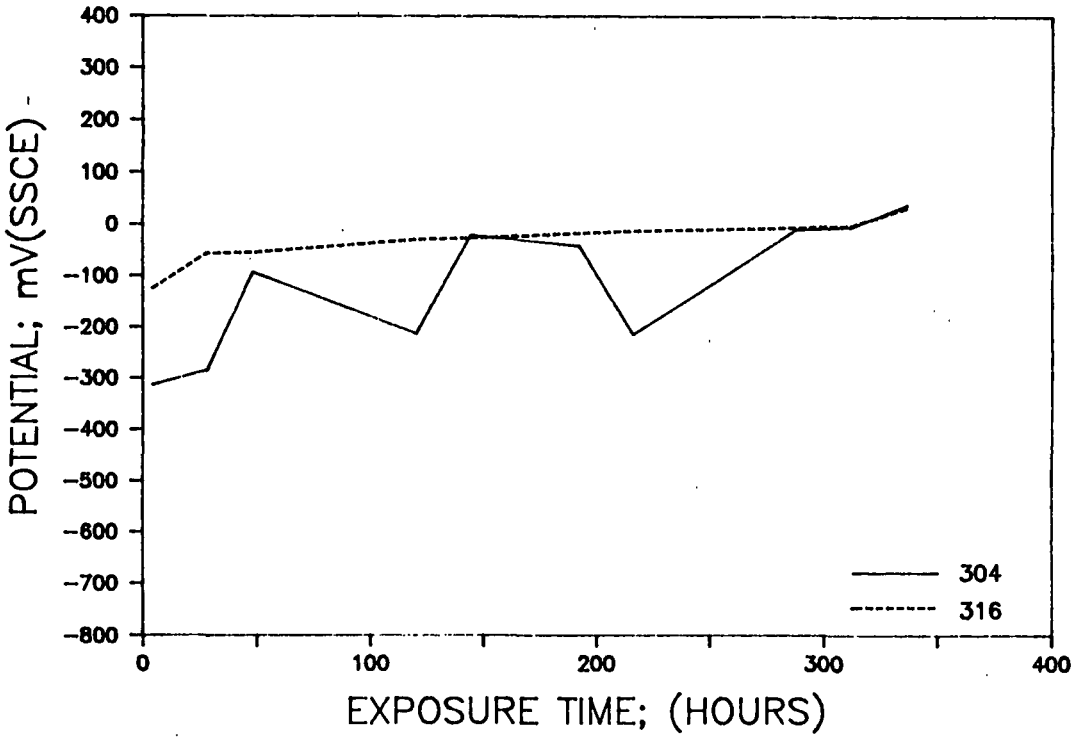

Figure A25. Corrosion potential versus time of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 10, 90°C.

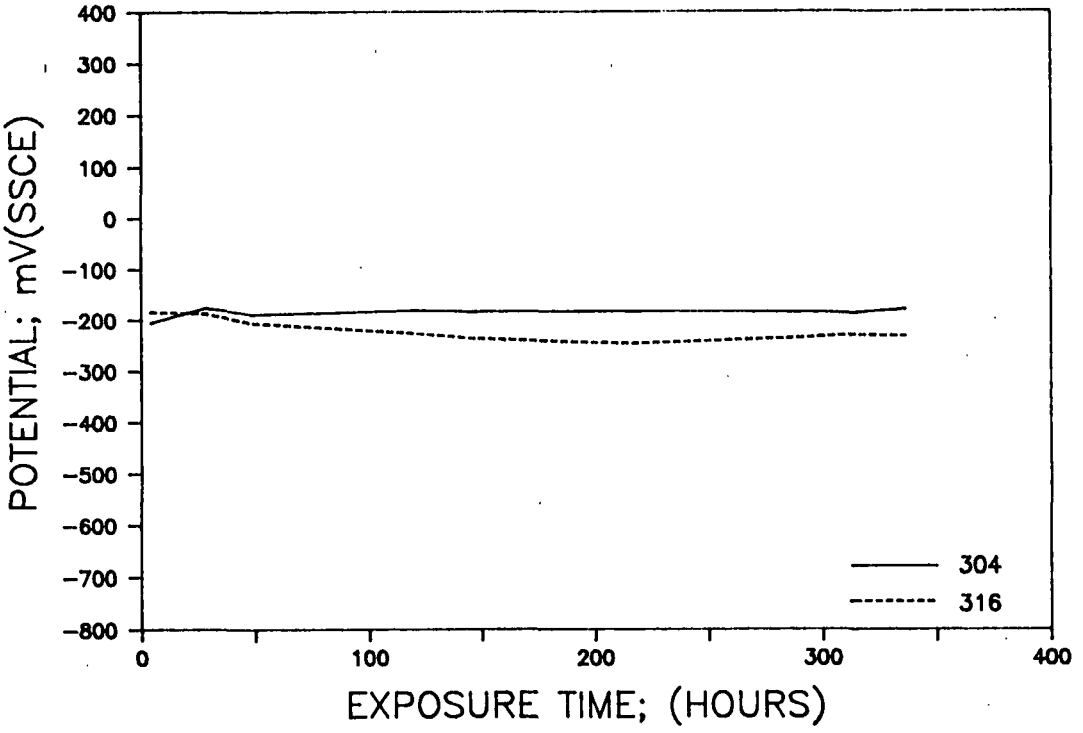

Figure A26. Corrosion potential versus time of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 7, 90°C.

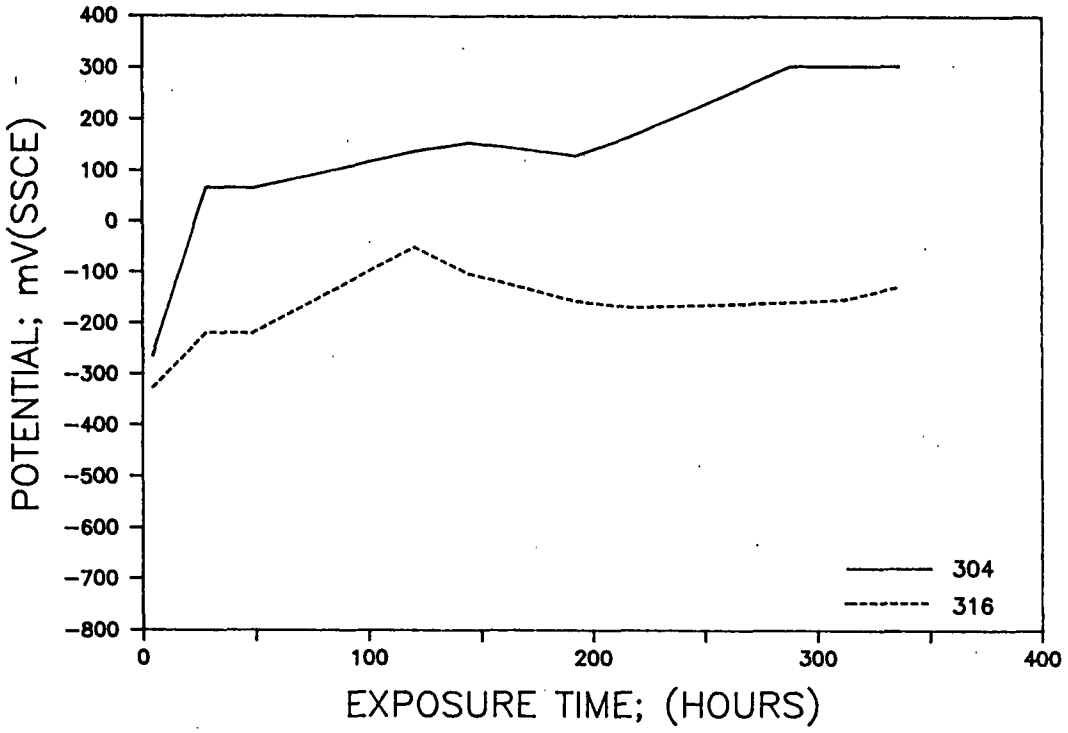

Figure A27. Corrosion potential versus time of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 4, 90°C.

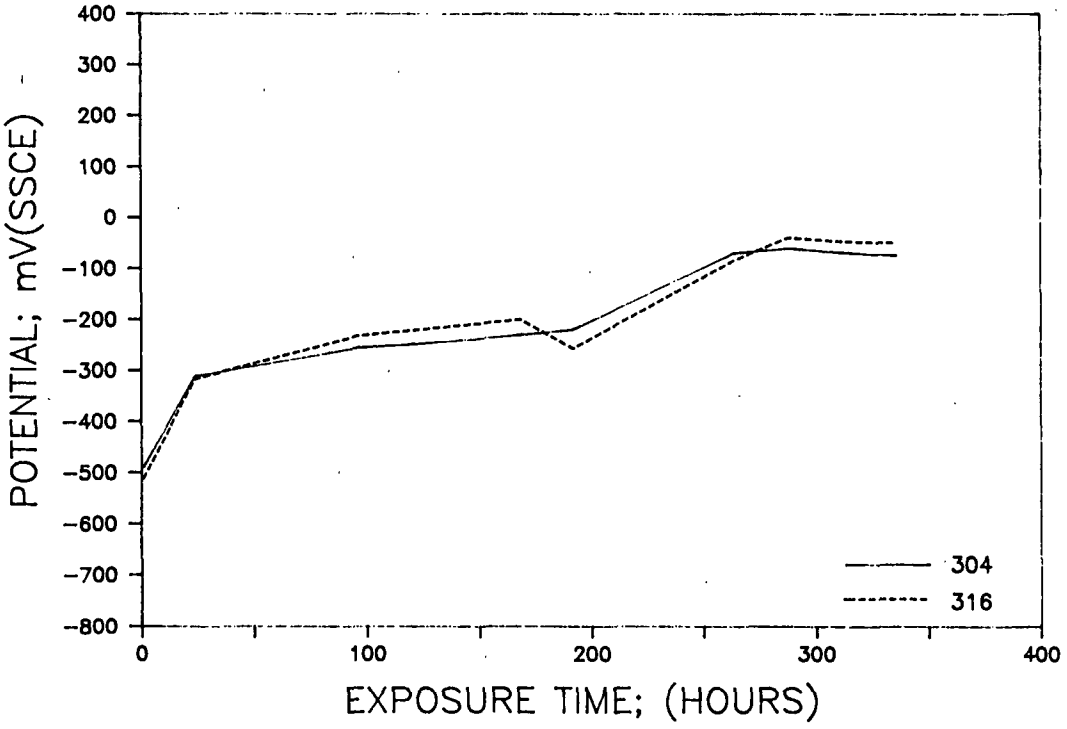

Figure A28. Corrosion potential versus time of 304 and 316 stainless steels. 6 g/L Na_2SO_3, pH 10, 90°C, solutions exposed to air.

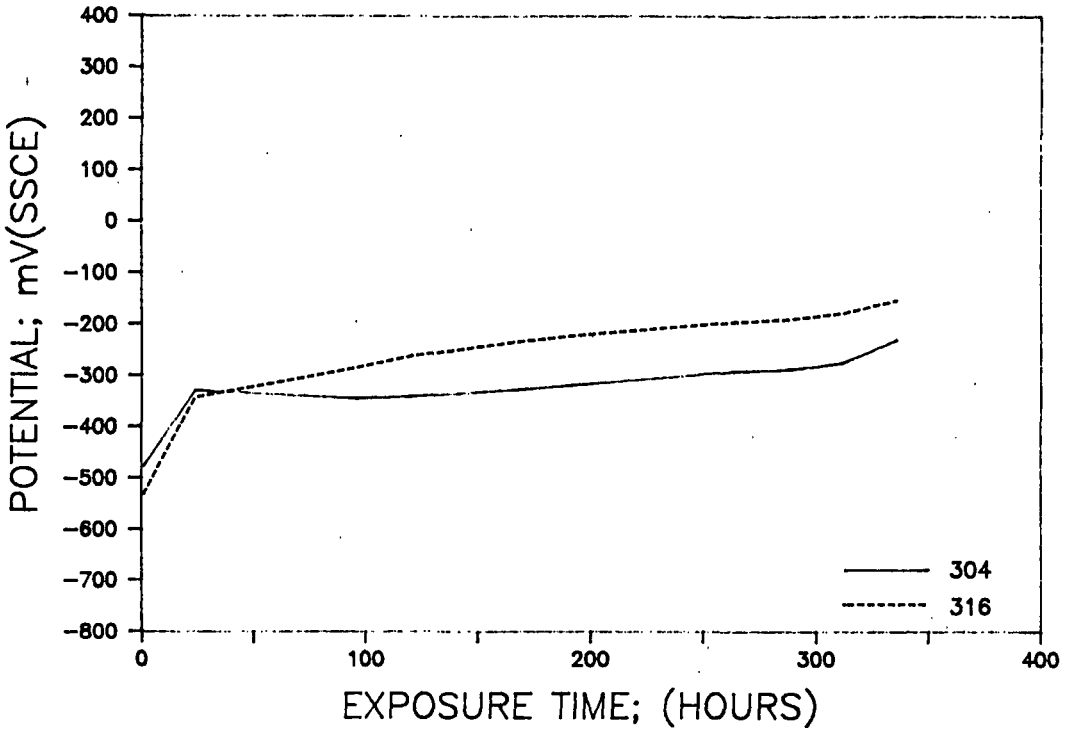

Figure A29. Corrosion potential versus time of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3, pH 10, 90°C, solutions exposed to air.

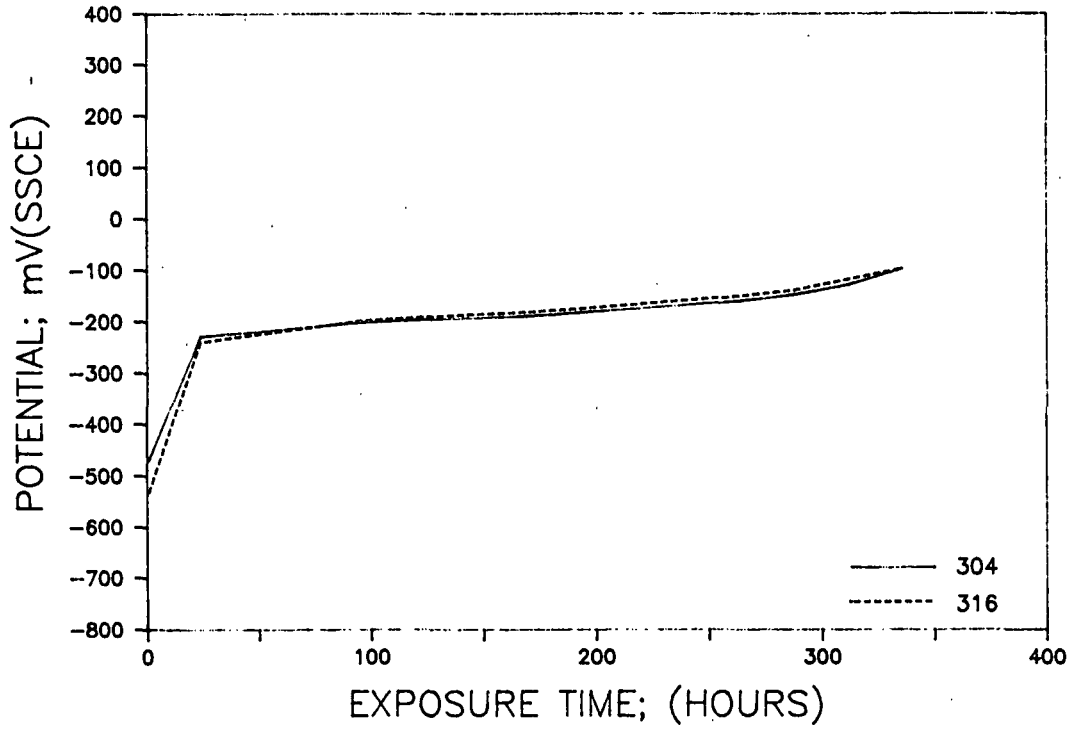

Figure A30. Corrosion potential versus time of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3, pH 7, 90°C, solutions exposed to air.

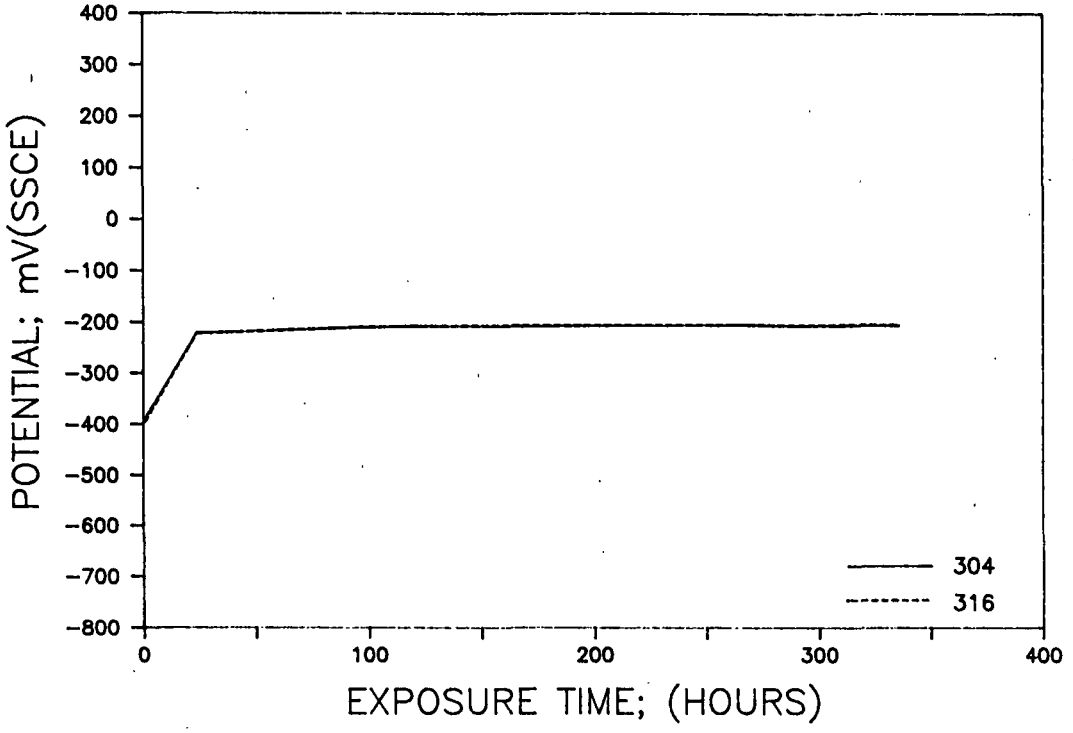

Figure A31. Corrosion potential versus time of 304 and 316 stainless steels. 59 g/L Na_2SO_3, pH 7, 90°C, solution exposed to air.

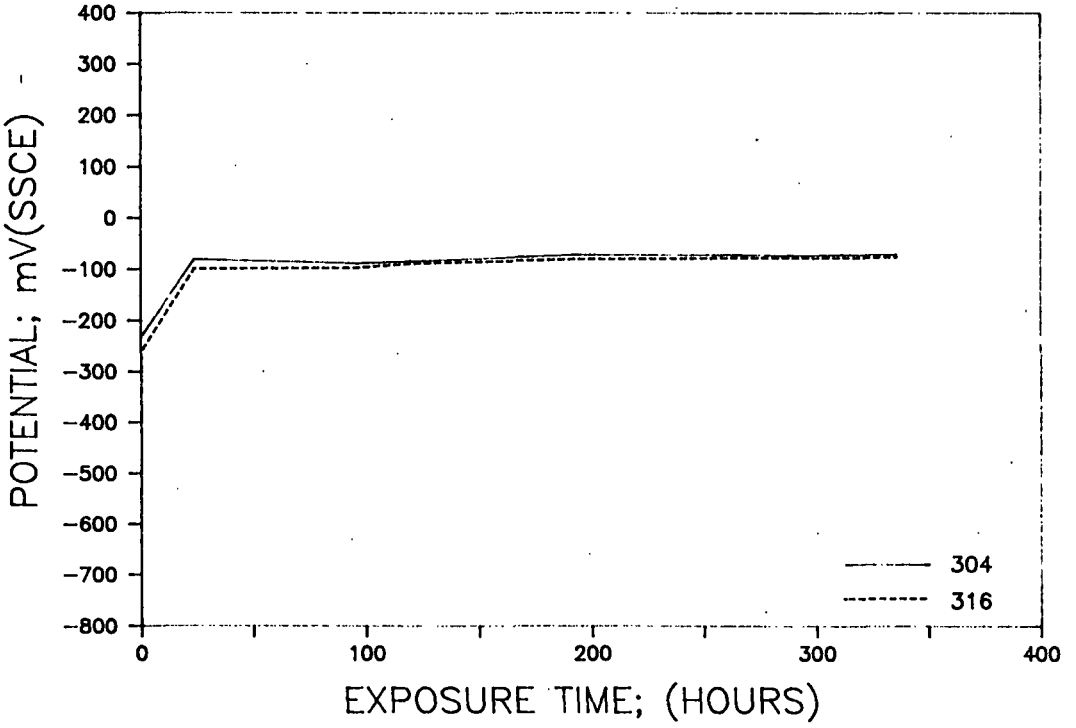

Figure A32. Corrosion potential versus time of 304 and 316 stainless steels. 10 g/L Na_2SO_3, pH 4, 90°C, solutions exposed to air.

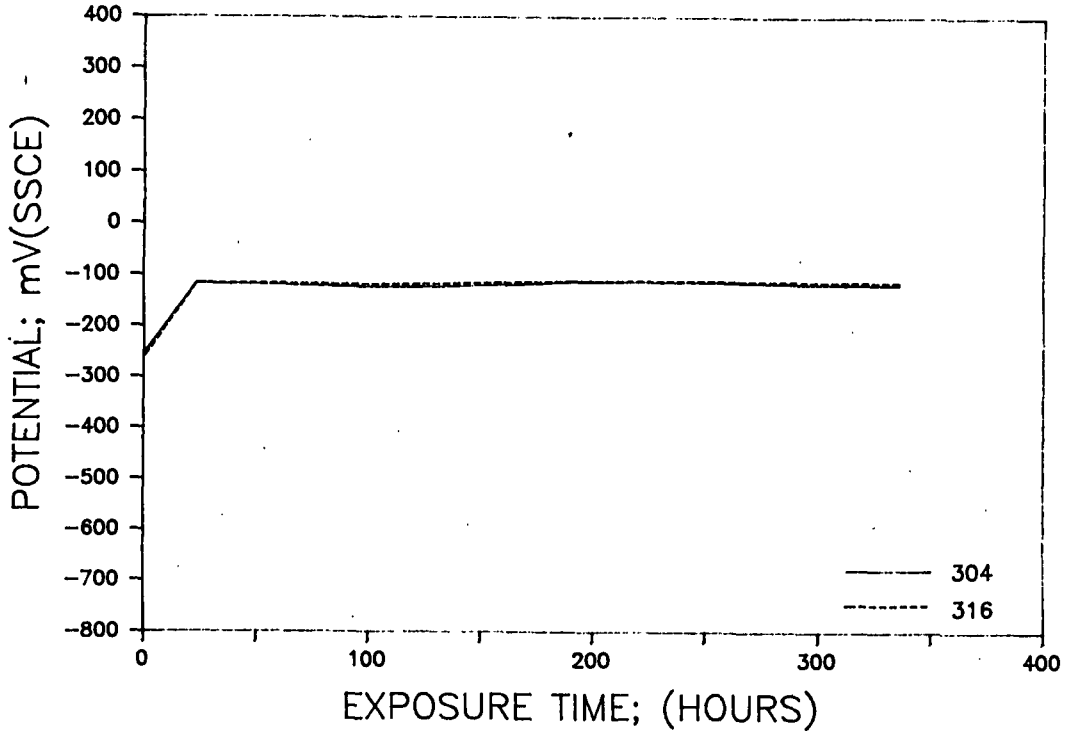

Figure A33. Corrosion potential versus time of 304 and 316 stainless steels. 26 g/L Na_2SO_3, pH 4, 90°C, solutions exposed to air.

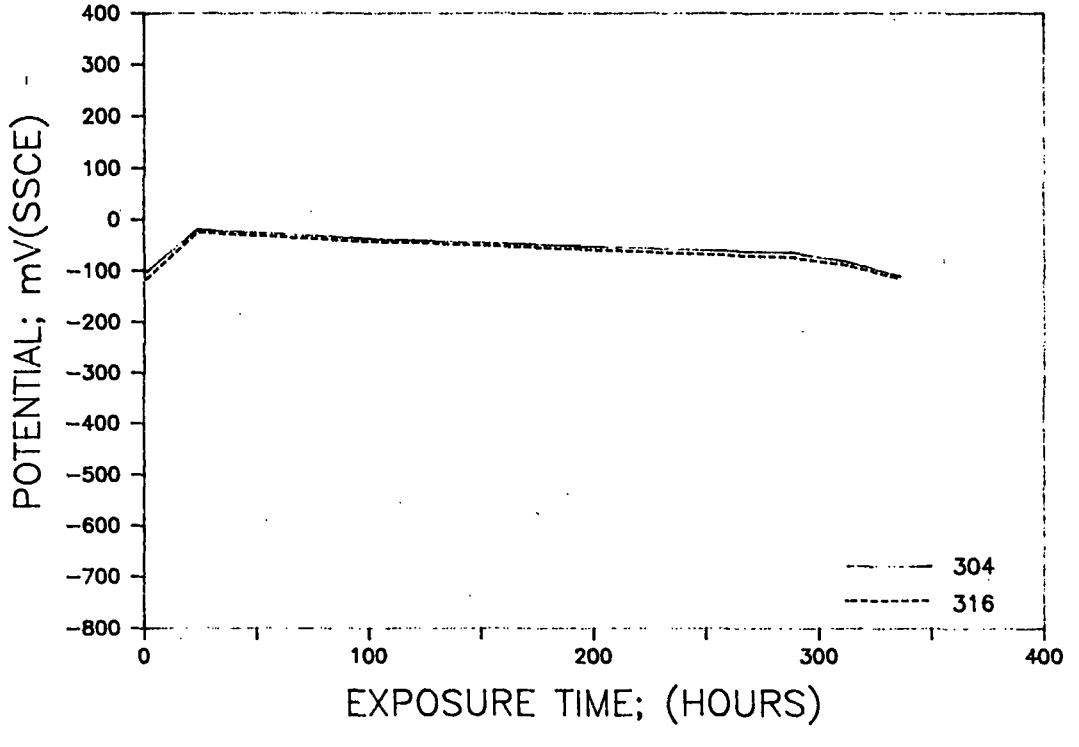

Figure A34. Corrosion potential versus time of 304 and 316 stainless steels. 52.5 g/L Na_2SO_3, pH 1.5, 90°C, solution exposed to air.

APPENDIX B

POLARIZATION BEHAVIOR AND POTENTIAL DECAY AT 150°C

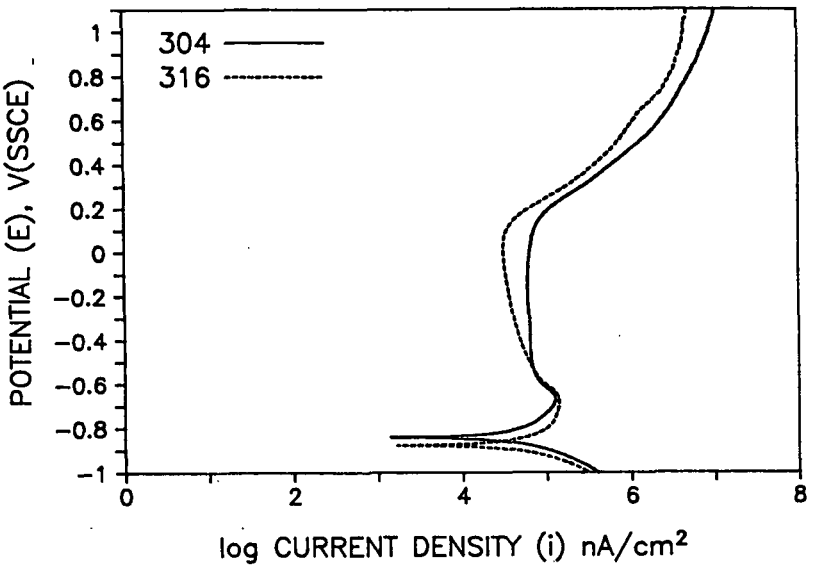

Figure B1. Polarization behavior of 304 and 316 stainless steels. 6 g/L Na_2SO_3, pH 10, 150°C.

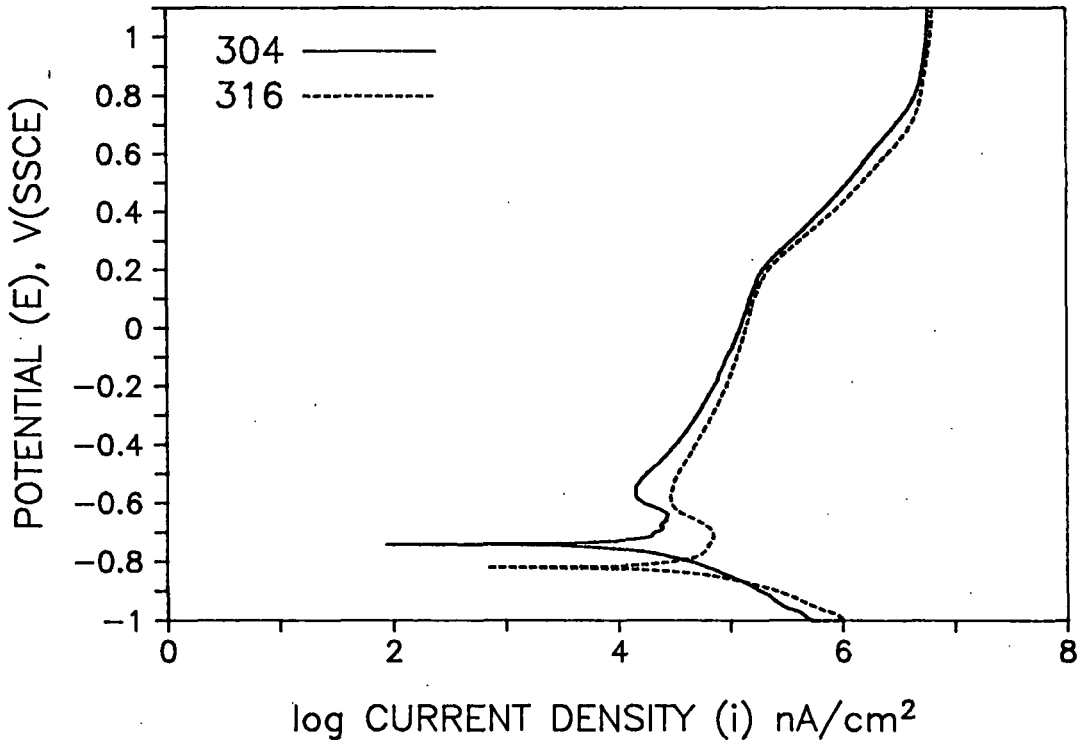

Figure B2. Polarization behavior of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3, pH 10, 150°C.

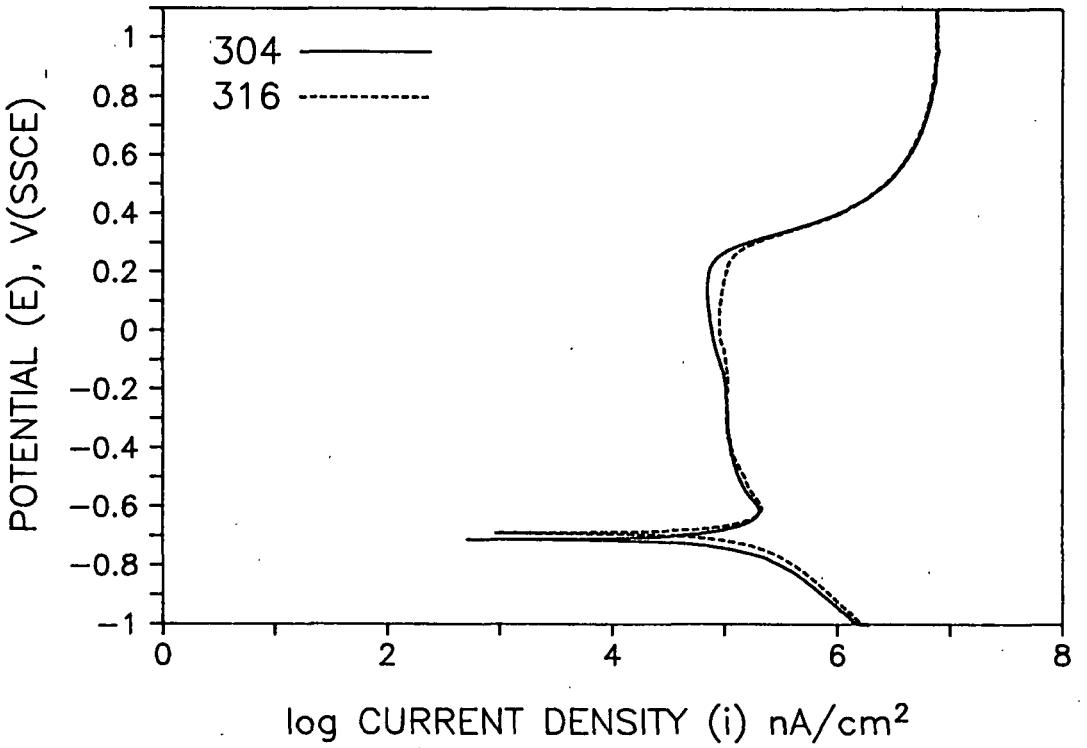

Figure B3. Polarization behavior of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3, pH 7, 150°C.

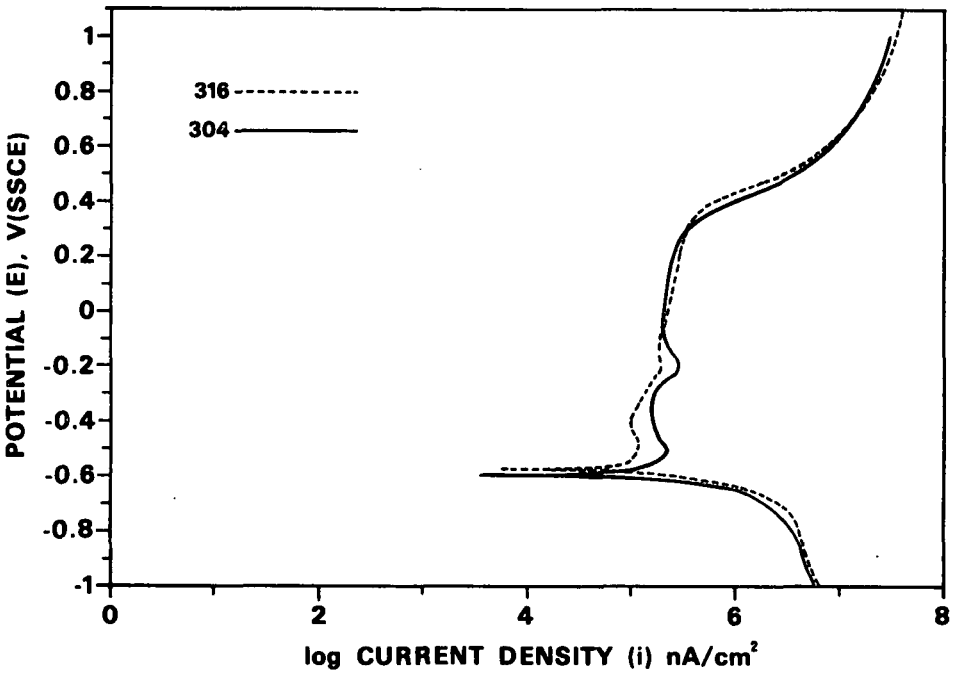

Figure B4. Polarization behavior of 304 and 316 stainless steels. 59 g/L Na_2SO_3, pH 7, 150°C.

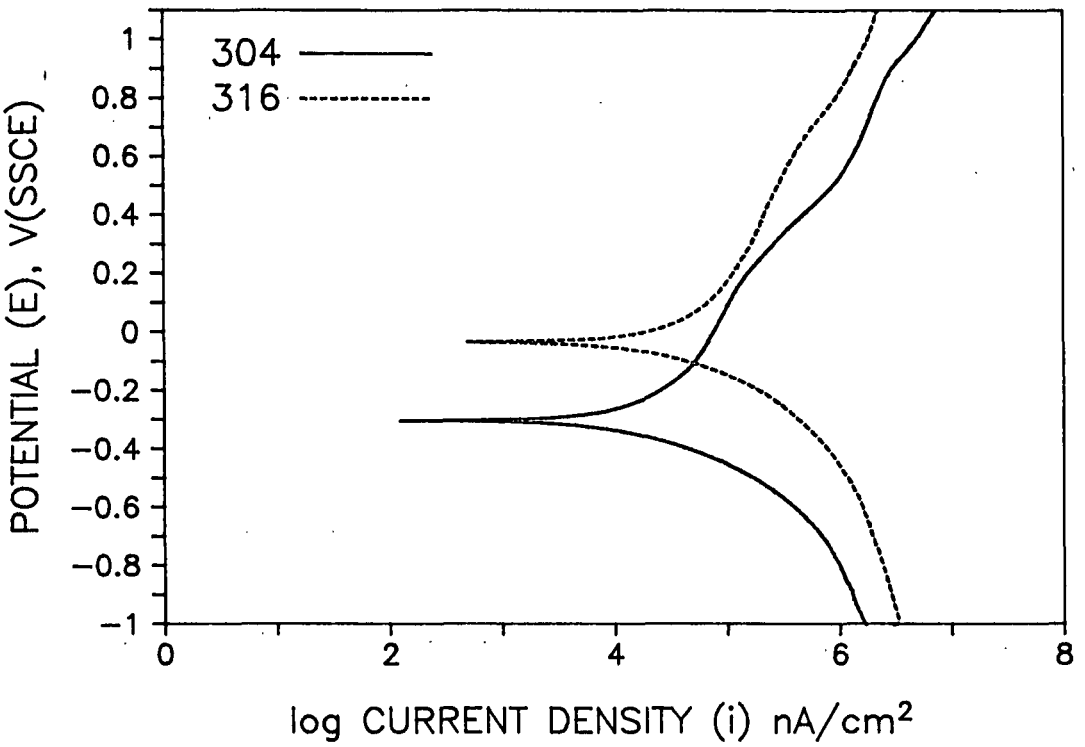

Figure B5. Polarization behavior of 304 and 316 stainless steels. 10 g/L Na_2SO_3, pH 4, 150°C.

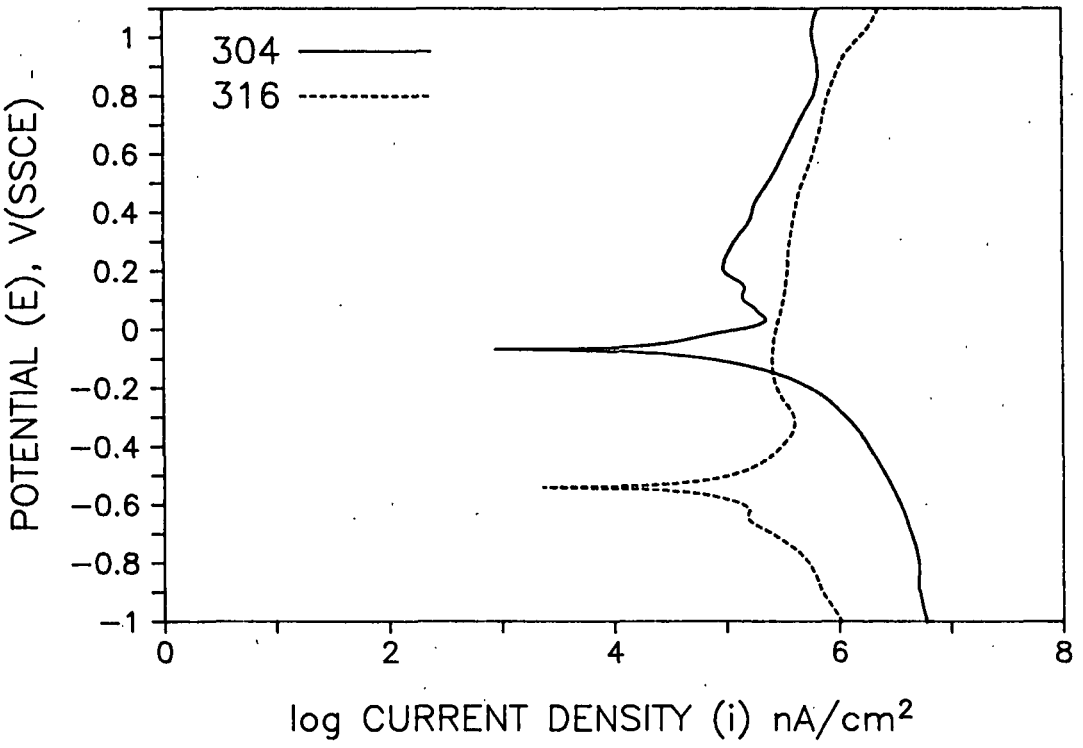

Figure B6. Polarization behavior of 304 and 316 stainless steels. 26 g/L Na_2SO_3, pH 4, 150°C.

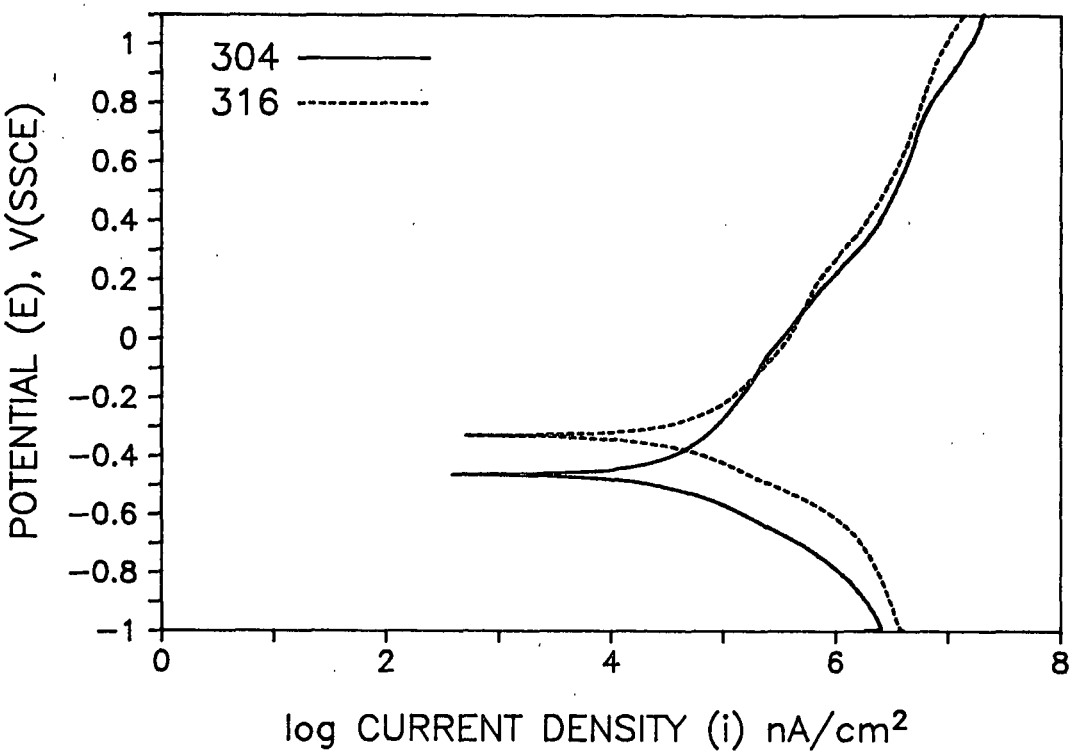

Figure B7. Polarization behavior of 304 and 316 stainless steels. 52.5 g/L Na_2SO_3, pH 1.5, 150°C.

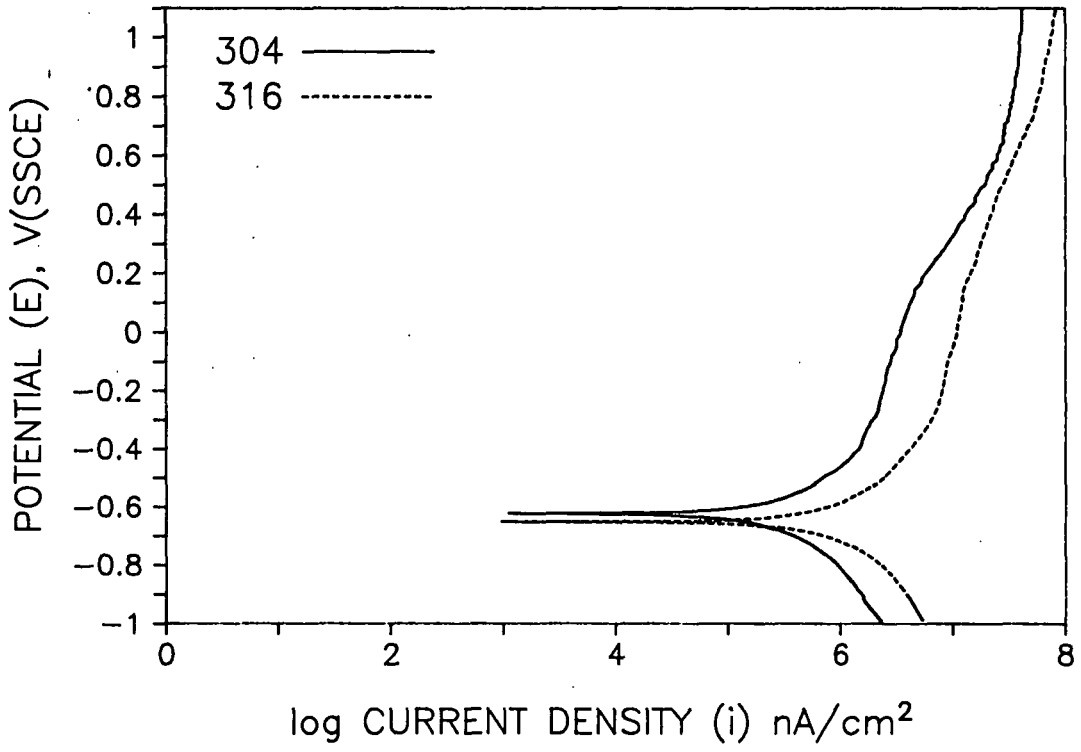

Figure B8. Polarization behavior of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3 + 1 g/L NaCl, pH 10, 150°C.

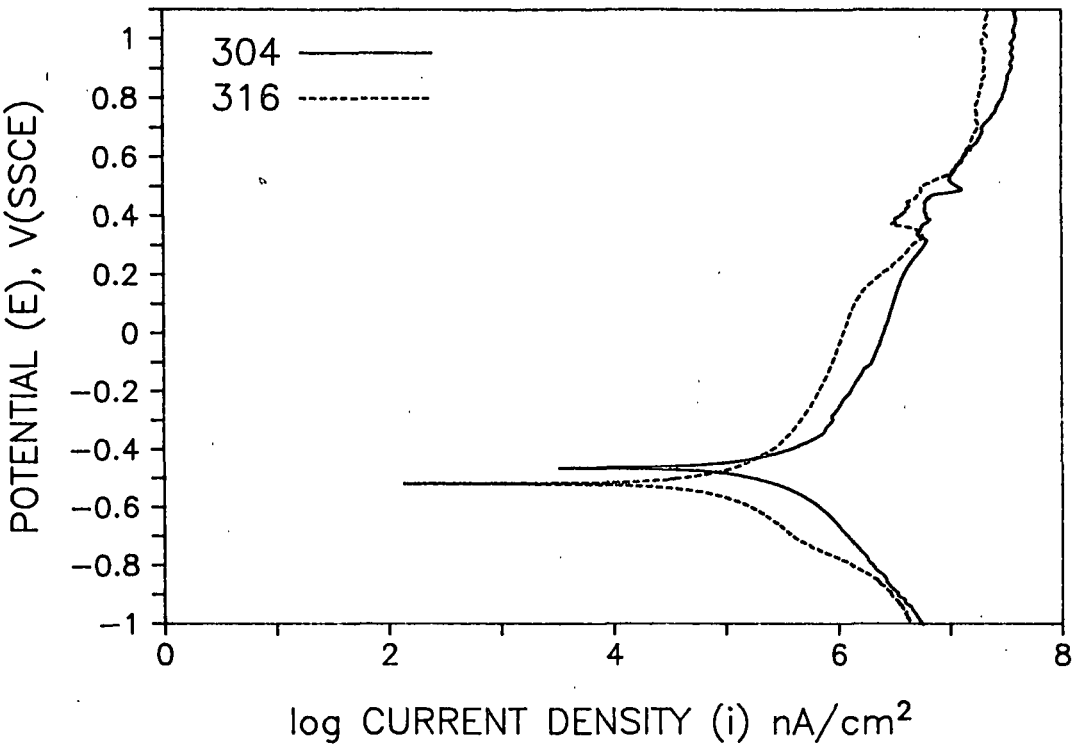

Figure B9. Polarization behavior of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3 + 1 g/L NaCl, pH 7, 150°C.

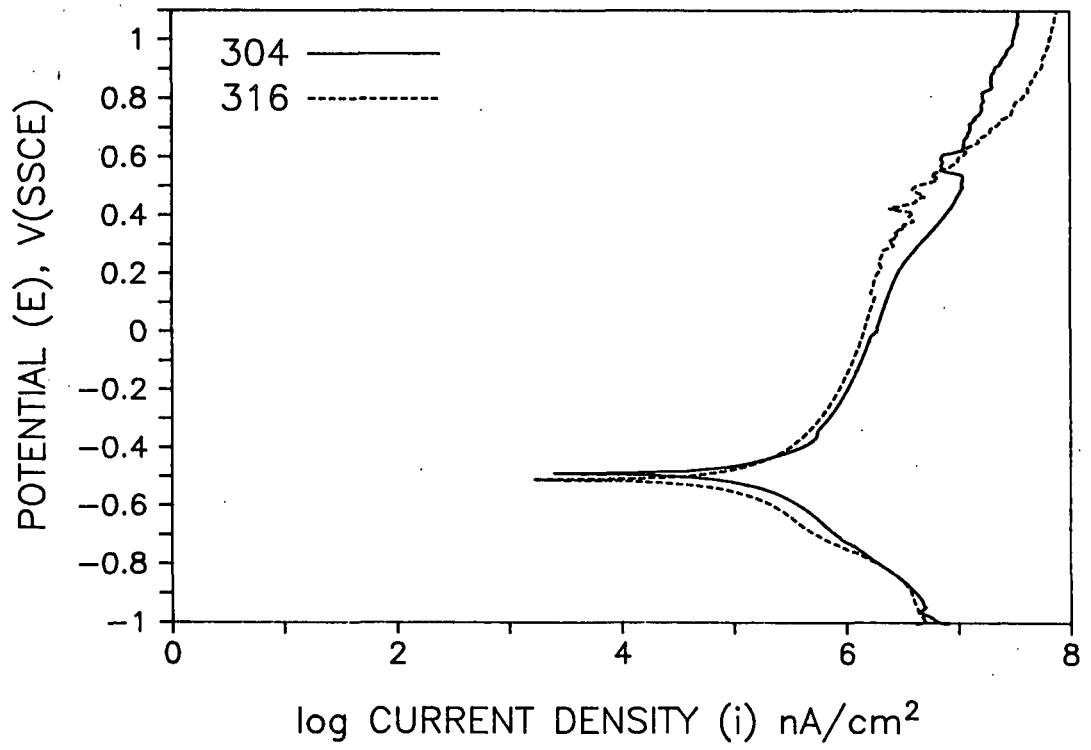

Figure B10. Polarization behavior of 304 and 316 stainless steels. 59 g/L Na_2SO_3 + 1 g/L NaCl, pH 7, 150°C.

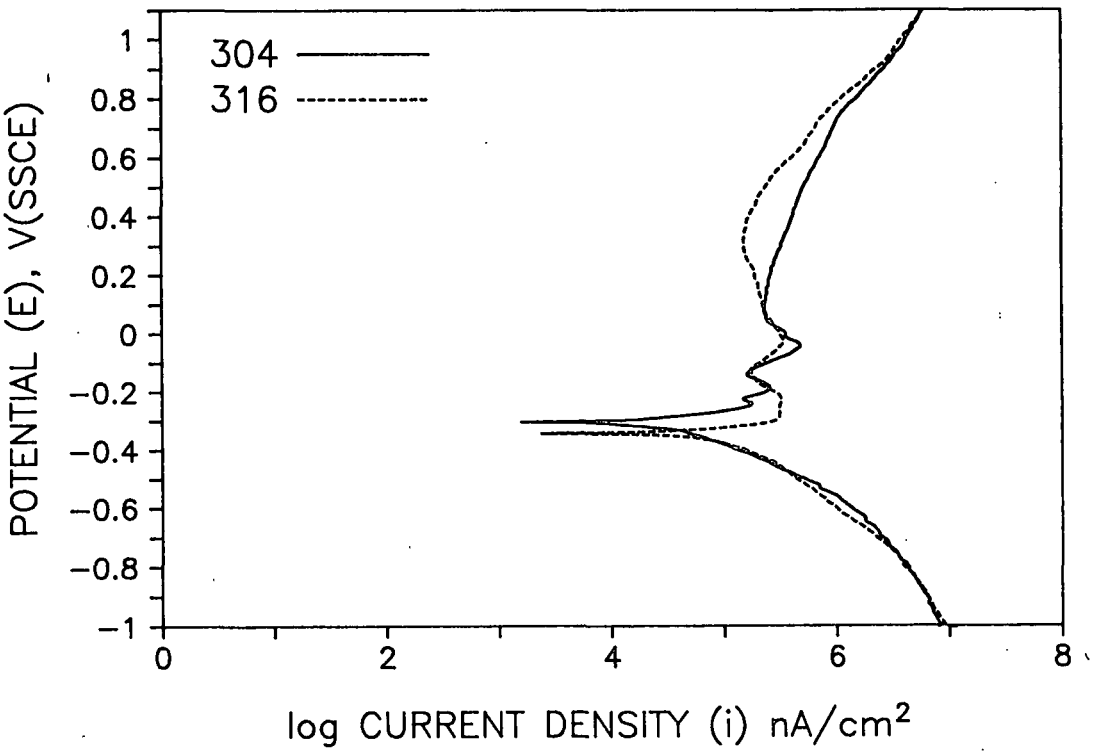

Figure B11. Polarization behavior of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 1 g/L NaCl, pH 4, 150°C.

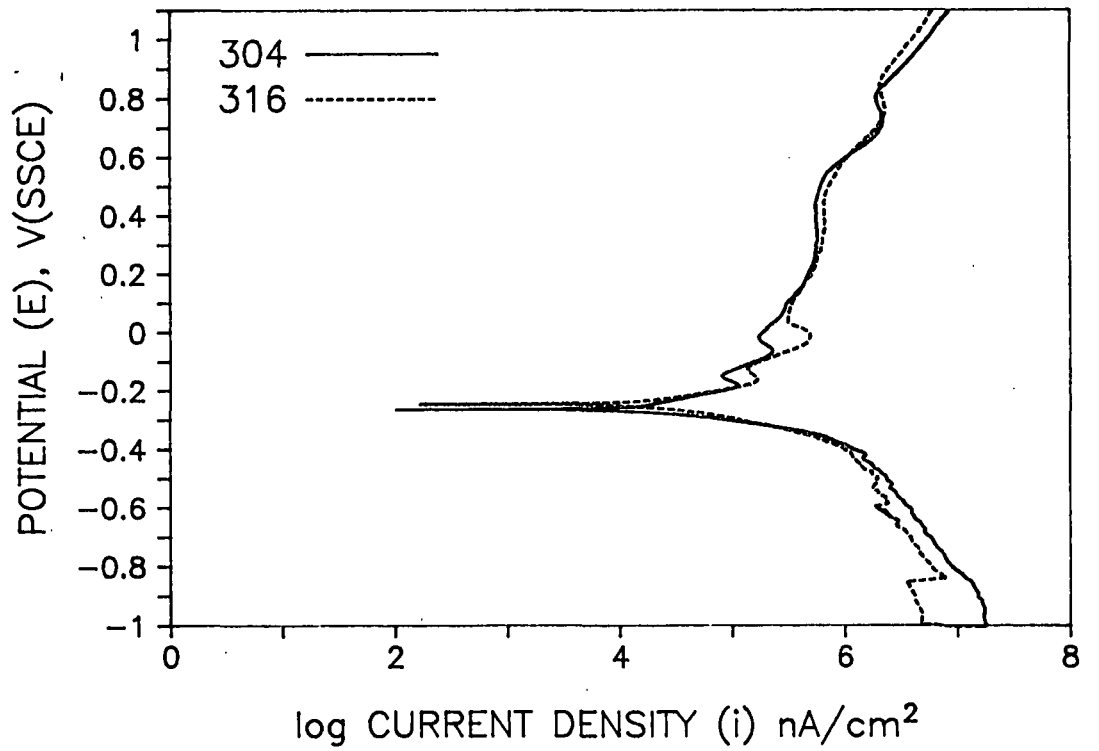

Figure B12. Polarization behavior of 304 and 316 stainless steels. 26 g/L Na_2SO_3 + 1 g/L NaCl, pH 4, 150°C.

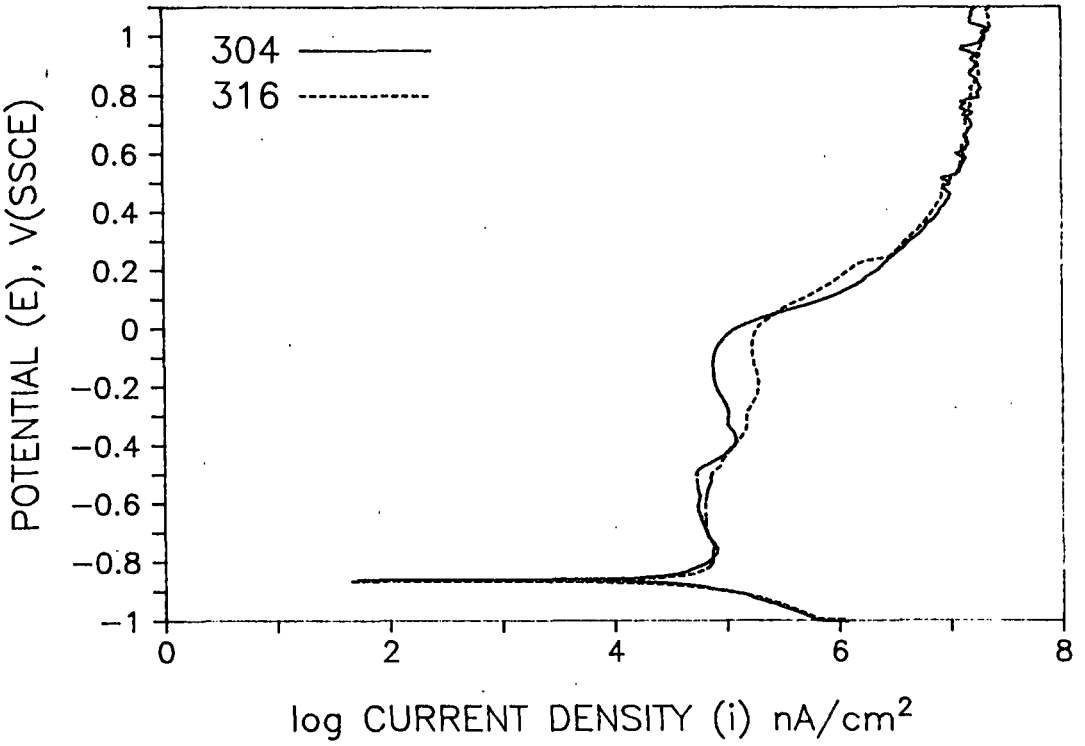

Figure B13. Polarization behavior of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 10, 150°C.

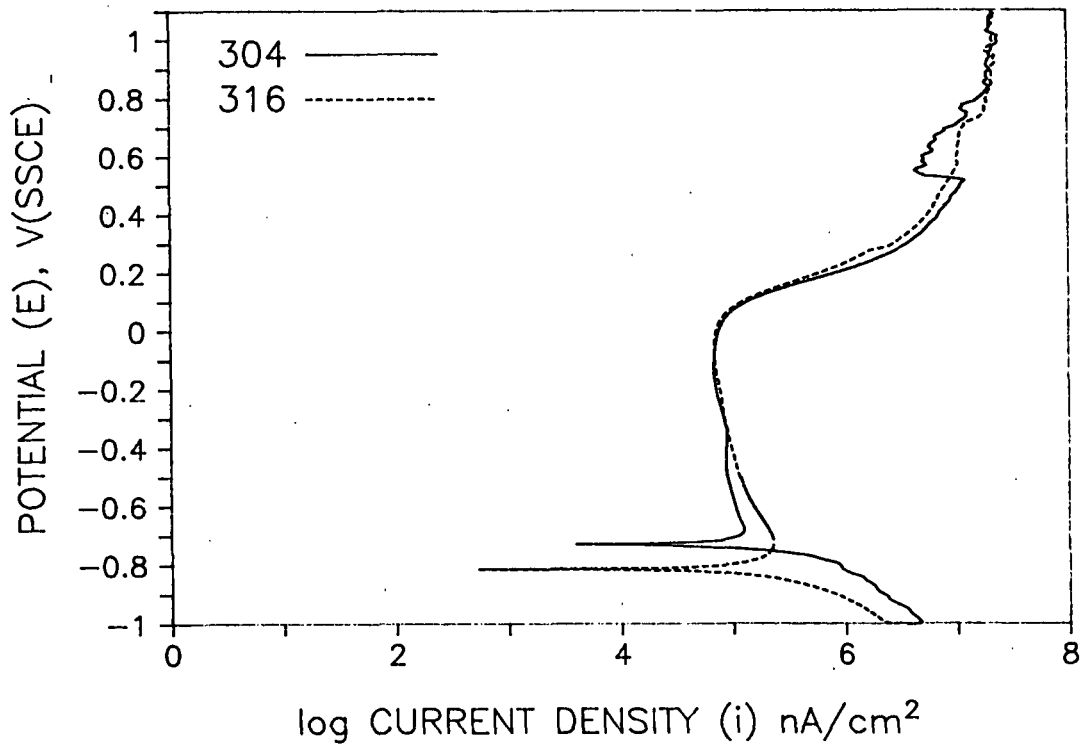

Figure B14. Polarization behavior of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 7, 150°C.

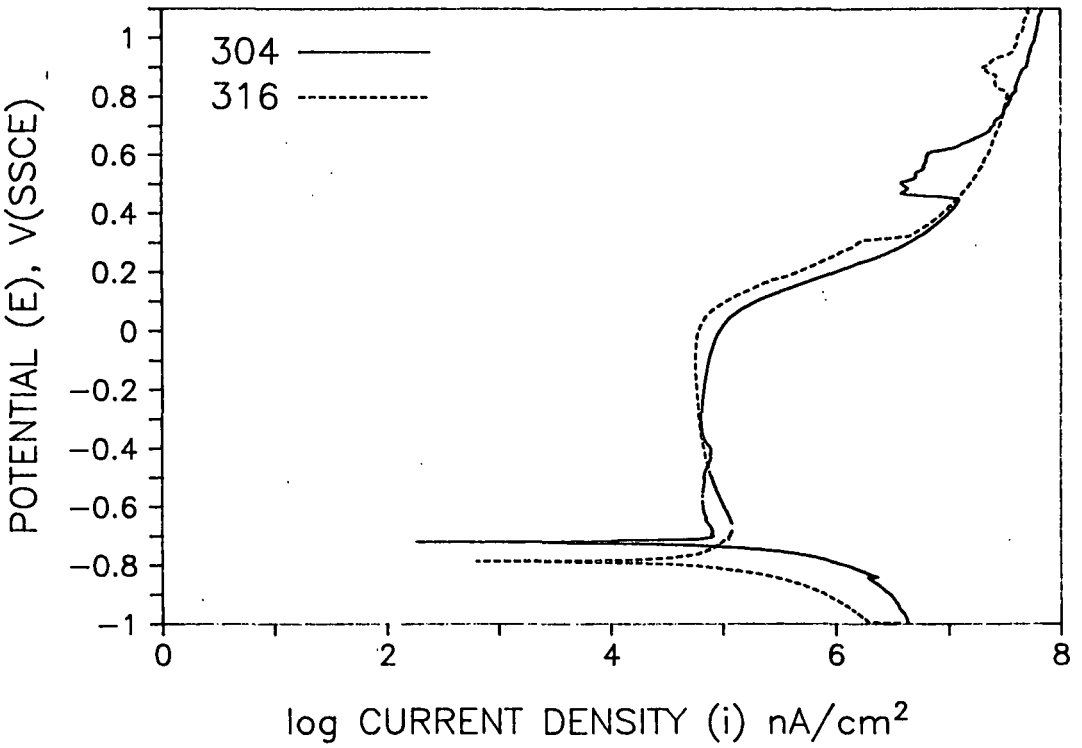

Figure B15. Polarization behavior of 304 and 316 stainless steels. 59 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 7, 150°C.

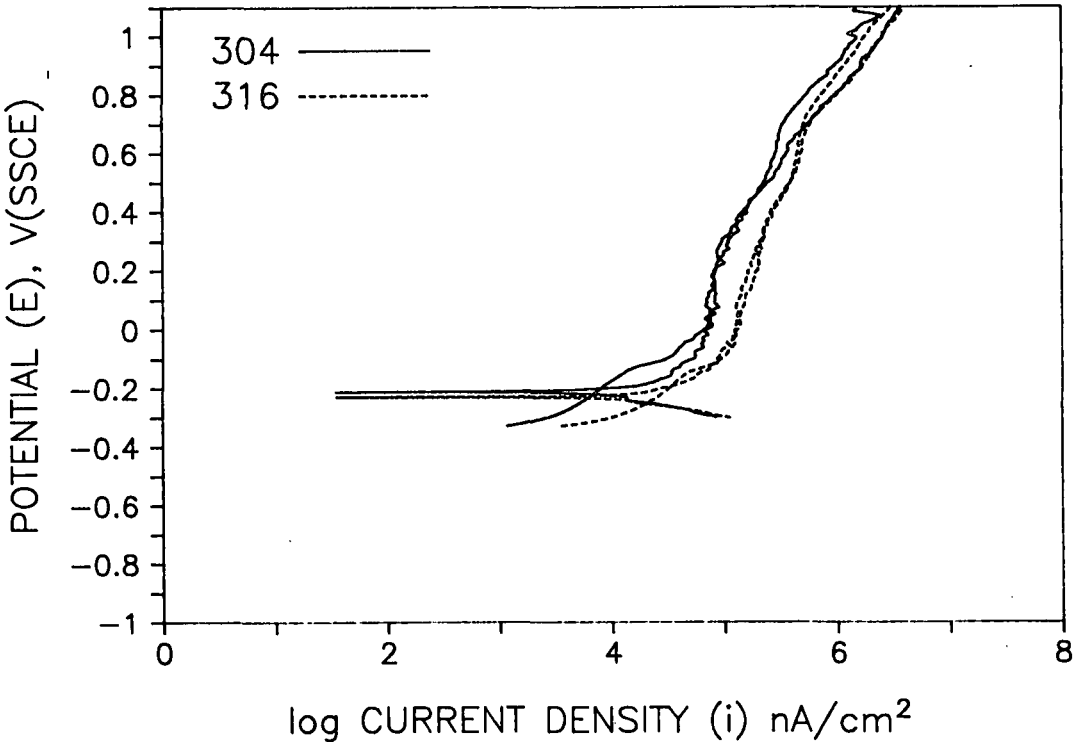

Figure B16. Polarization behavior of 304 and 316 stainless steels. 10 g/L Na_2SO_3 + 5 g/L $Na_2S_2O_3$, pH 4, 150°C.

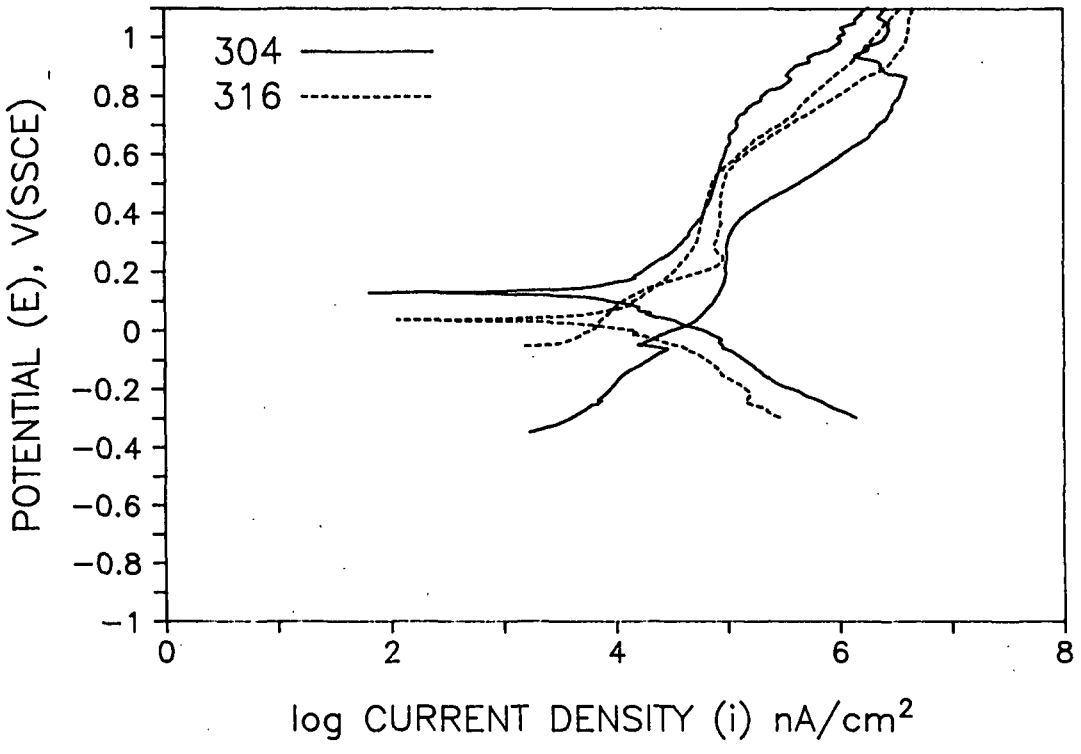

Figure B17. Polarization behavior of 304 and 316 stainless steels. 26 g/L $NaHSO_3$ + 5 g/L $Na_2S_2O_3$, pH 4, 150°C.

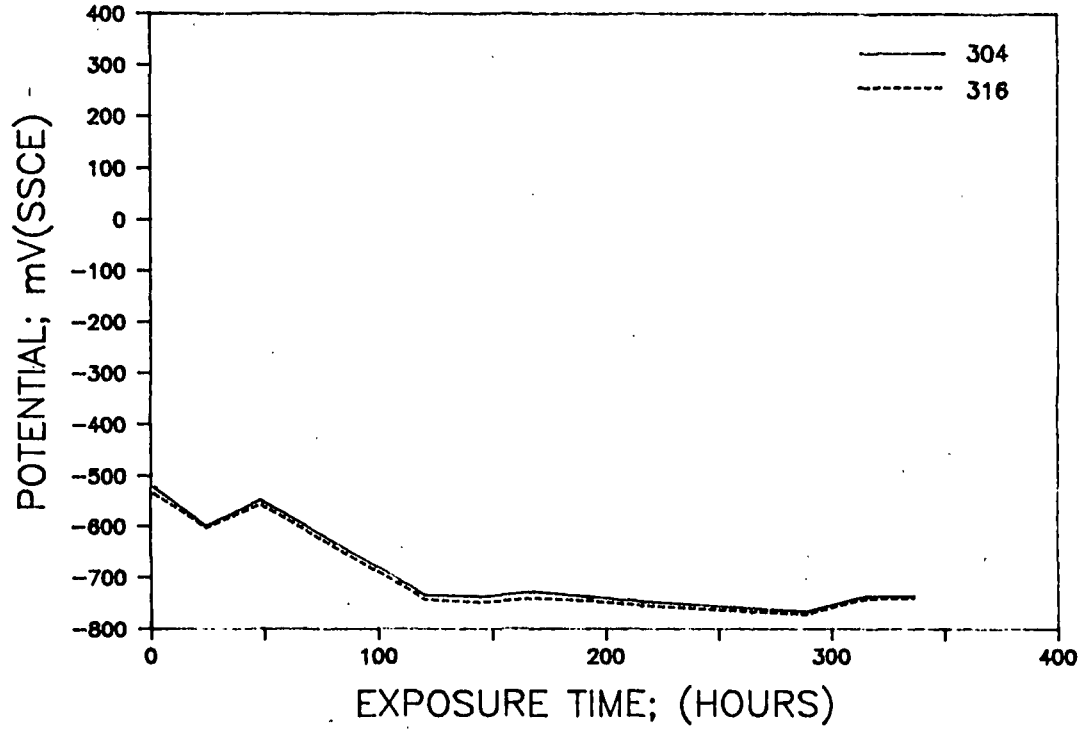

Figure B18. Corrosion potential versus time of 304 and 316 stainless steels. 6 g/L Na_2SO_3, pH 10, 150°C.

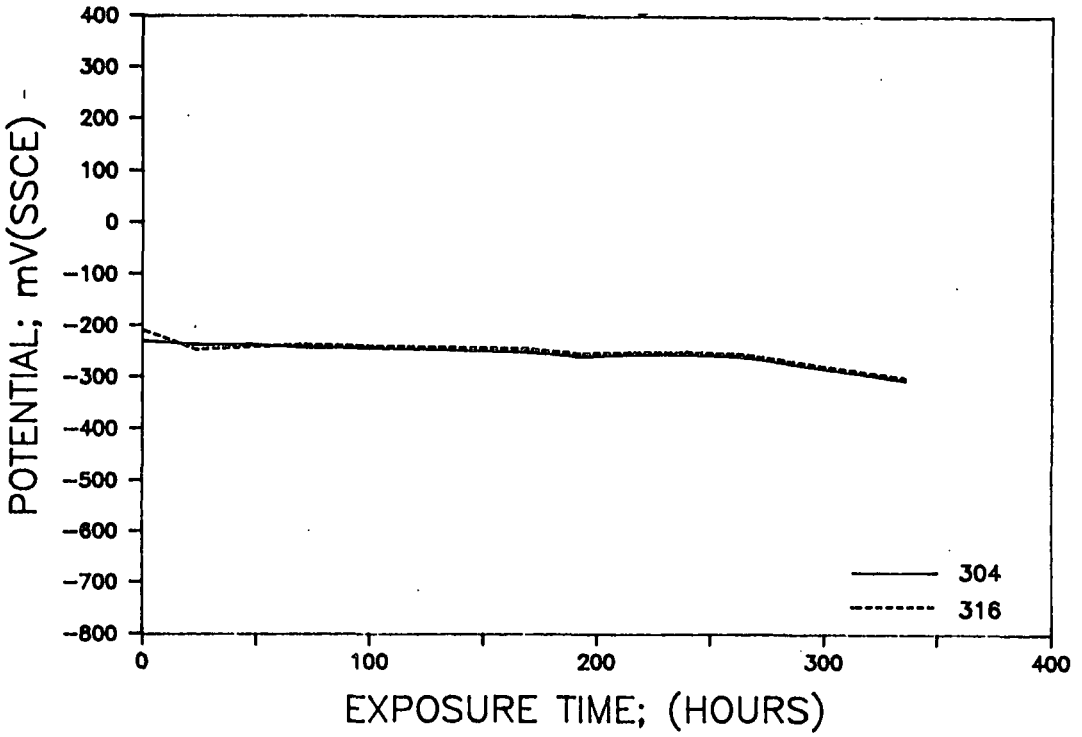

Figure B19. Corrosion potential versus time of 304 and 316 stainless steels. 8.5 g/L Na_2SO_3, pH 10, 150°C.

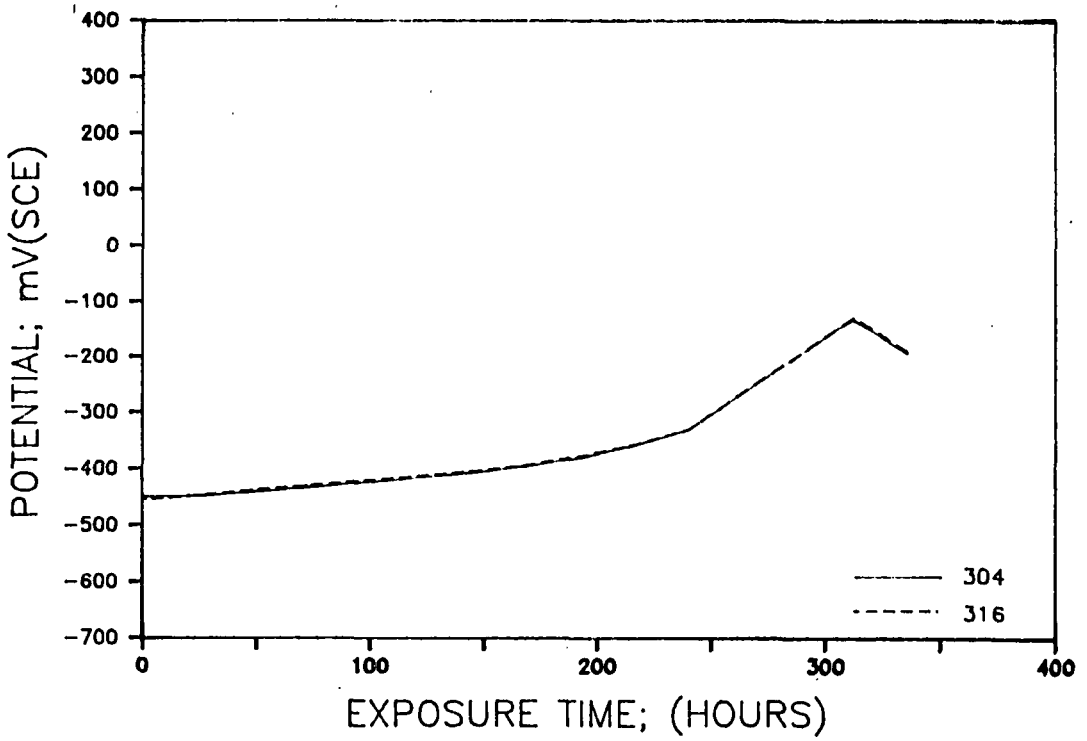

Figure B20. Corrosion potential versus time of 304 and 316 stainless steels. 16.5 g/L Na_2SO_3, pH 7, 150°C.

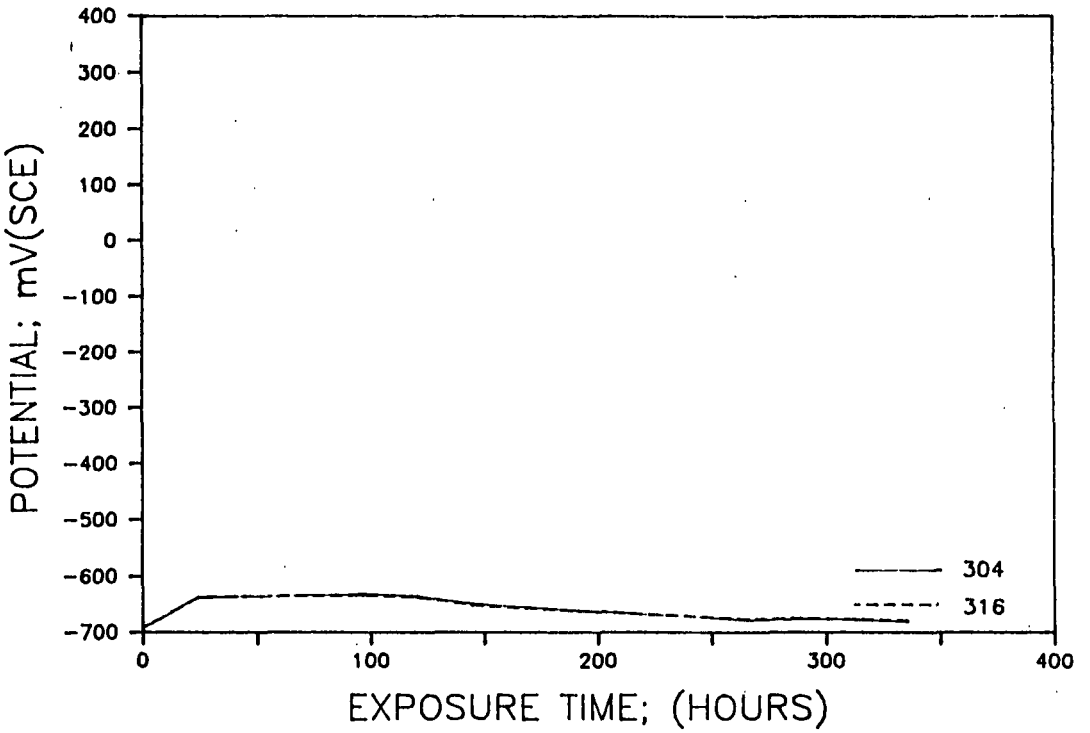

Figure B21. Corrosion potential versus time of 304 and 316 stainless steels. 59 g/L Na_2SO_3, pH 4, 150°C.